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ENVIRONMENTAL MONITORING NEAR INDUSTRIAL SITES : CHROMIUM

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16 ABSTRACT

A sampling and analysis program was conducted to determine concentrations of chromium in the air, water and soil in the environs of industrial sites and sewage treatment plants. Five industrial categories - chrome pigments producers, electroplating plants, ferrochromium plants, leather tanneries, and sodium dichromate/chromic acid producers - were presurveyed to select the final sampling sites.

Samples were gathered at two chrome pigment plants, an electroplating plant, a leather tannery and two sewage treatment plants. The protocol for sampling air utilized high-volume samplers in either a downwind array or in a plant perimeter geometry. Composite 24-hour water samples were taken and soil core samples were obtained.

The techniques employed for analysis of the environmental samples were intended to differentiate between the two most common chromium valence states (III and VI). This was accomplished for water samples but not for air, soil or sediment samples because acid digestion converted chromium (VI) to chromium (III). All analyses were obtained on a Varian AA-6 atomic absorption spectrometer.

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ENVIRONMENTAL MONITORING NEAR INDUSTRIAL SITES: CHROMIUM

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1. SUMMARY

A sampling and analysis program was conducted to determine concentrations of chromium in the air, water and soil in the environs of industrial sites and sewage treatment plants. Five industrial categories - chrome pigments producers, electroplating plants, ferrochromium plants, leather tanneries, and sodium dichromate/chromic acid producers - were presurveyed to select the final sampling sites.

Samples were gathered at two chrome pigment plants, an electroplating plant, a leather tannery and two sewage treatment plants. The protocol for sampling air utilized high-volume samplers in either a downwind array or in a plant perimeter geometry. Composite 24-hour water samples were taken and soil core samples were obtained.

The techniques employed for analysis of the environmental samples were intended to differentiate between the two most common chromium valence states (III and VI). This was accomplished for water samples but not for air, soil or sediment samples because acid digestion converted chromium (VI) to chromium (III). All analyses were obtained on a Varian AA-6 atomic absorption spectrometer.

2. IDENTIFICATION OF SAMPLING LOCATIONS

2.1 POSSIBLE SOURCES OF CHROMIUM EMISSIONS IN INDUSTRY

Industrial emission of chromium occurs during activities directly associated with the rendering of chromium ores and their subsequent fabrication or chemical conversion into useful products, and during high-volume processes such as combustion of coal. The importance of these types of emissions to the local, regional or global environment depends on the chemical and physical form of the chromium in the emission, the environmental medium (air, water, soil) into which the emission occurs, the average and peak concentration of emission, the geographical relationship of the emission site to populations of organisms, especially humans, and other factors. Lists of likely sampling sites were prepared based on an analysis of the industrial flux of chromium. A manageable number of sites was selected for sampling through a process of site visits and telephone contacts.

2.1.1 Incidental Chromium Emissions

The combustion of coal (1) and the production of iron are two industrial activities in which large volumes of minerals are processed. Trace elements are frequently released in large

(1) Duprenant, Norman, Robert Hall, Steven Slater, Thomas Busa, Martin Sussman and Charles Young. "Preliminary Emissions Assessment of Conventional Stationary Combustion Systems," EPA 600/2-76-046b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1976, p. 79.

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quantities to the environment during these processes. In the case of volatile elements like mercury these processes represent a major mechanism for release of the elements from the lithosphere to the biosphere (i.e., atmosphere). Refractory elements such as chromium are also released, usually in the form of glassy fly ash where metals are bound as counterions for the polysilicate matrix.

The highly diluted nature of these incidental emissions and the wide geographic dispersal of these industries tend to preclude the exposure of any population group to serious levels of any one trace element. For example, the exact form of chromium in fly ash is unknown; as noted above, it is likely to have low bioavailability. Assume that all of the chromium in fly ash was in the form of the rather toxic and corrosive chromic(VI) acid for which the threshold limit value (TLV®) is 0.1 mg/m^3. A sample calculation (2) for a coal-fired utility boiler (capacity = 400 MW, stack height = 82 m, chromium content of coal = 15 ppm, uncontrolled chromium emission factor = 90% of chromium content, control efficiency = 80%, plant heat rate = 2.98 J(coal input)/J(power output), coal heat content = 25.8 x 10^6 J/kg) yields a maximum chromium ground level concentration (x_{max}) of 1 µg/m^3. This is a factor of 100 below the TLV for chromic(VI) acid.

Thus, incidental emissions will not be considered because they do not present a critical situation which demands immediate concern.

2.1.2 Emissions From the Chromium Industry

The consumption and uses of chromium in the U.S. economy are shown in Figure 1. Symbols are used in Figure 1 to designate

(2) Resnik, Richard D. "Source Assessment: Flat Glass Manufacturing Plants," EPA 600/2-76-032b, March 1976, pp 122-126.

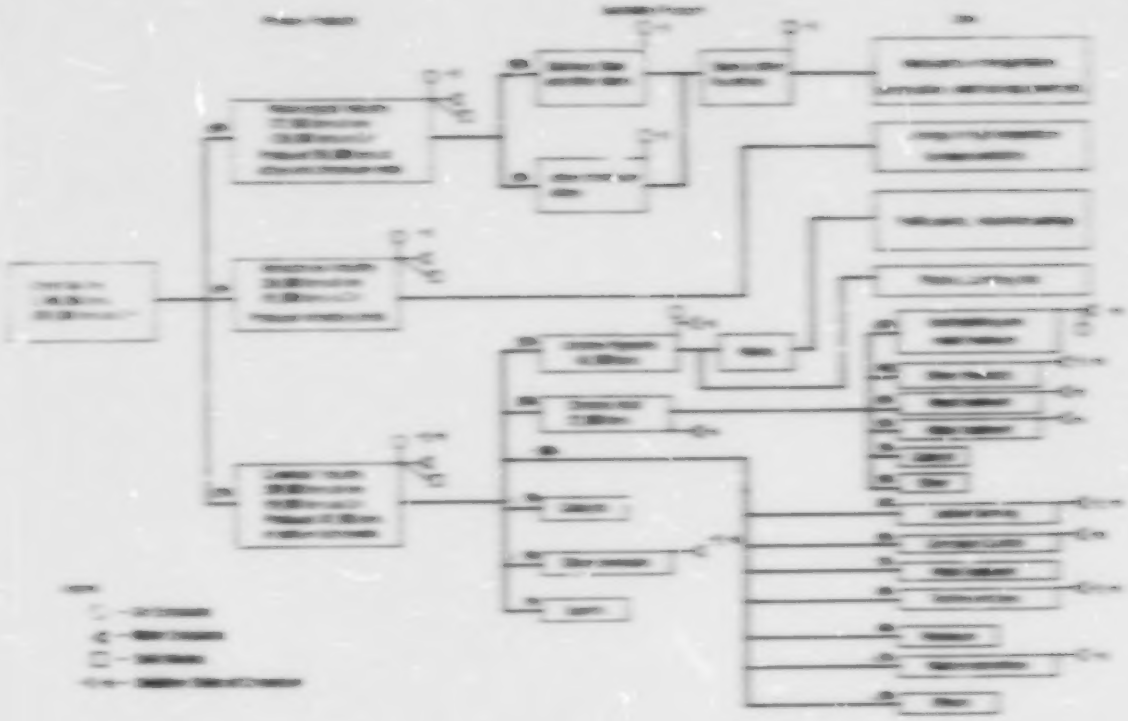

Figure 1. Consumption and Uses of Chromium.

operations which give rise to air emissions (a), water emissions (d), and solid wastes (3). A number (3 or 6) indicates whether chromium is present in the trivalent or hexavalent form.

Chromium is one of the few elements for which the U.S. is almost totally dependent upon imports. Imported chromite ore ($Cr_2O_3.FeO$) is converted into three primary products: ferrochromium (68%), refractory brick (16%), and sodium dichromate (17%). Ferrochromium is converted primarily to steel (92%) or other alloys. The chrome refractories are used as linings in high temperature furnaces or kilns. Sodium dichromate finds direct use in some applications, while in other cases it is first converted to another chromium compound. Some of the more significant emission sources based on Figure 1 are listed below.

- Metallurgical Industries

  Chromite ore is reduced with coke in an electric arc furnace to give ferrochromium. Uncontrolled emissions have been reported from 100 g/kg to 415 g/kg, but the majority of the industry (>80%) has installed controls (typically 95% efficient). Ferrochromium plants are listed in Table 1.

Table 1. FERROCHROMIUM PLANTS

Company	Plant Location
Airco Alloys and Carbide Div.; Air Reduction Co. Inc.	Calvert City, Ky.; Niagara Falls, N.Y.; Charleston, S.C.
Chromium Mining and Smelting Corp.	Woodstock, Tenn.
Foote Mineral Co.	Graham, W. Va.
Interlake Inc.	Beverly, Ohio
Ohio Ferro-Alloys Corp.	Brilliant, Ohio
Shieldalloy Corp.	Newfield, N.J.
Union Carbide Corp.	Niagara Falls, N.Y. Marietta, Ohio

Ferrochromium is used primarily in the production of stainless steels. Uncontrolled furnace emissions from this process average 12 g/kg. The level of control is similar to that in the ferrochromium industry.

In the metallurgical industries, chromium is emitted to the atmosphere as chromium(III) oxide along with other metal oxides, and particulates are often below 1 micron in size. Wet scrubbers used for emissions control produce a water effluent containing chromium.

Refractories Industries

Chromite grinding will generate fugitive dust, but particles in the respirable range should amount to ~1 g/kg or less compared to emissions of ~100 g/kg from ferrochrome furnaces.

The Chemical Industries

(A) Sodium Dichromate - Chromite ore is roasted in a rotary kiln with soda ash or lime to form a soluble chromate. This is leached, precipitated, and dried as sodium dichromate. The compound is made at three plants, listed in Table 2, which have controls for air and water emissions.

Table 2. SODIUM DICHROMATE PLANTS

Company	Plant Location	Capacity (metric tons/yr)
Allied Chemical Corp.	Baltimore, Md.	68,000
Diamond Shamrock Corp.	Castle Haynes, N.C.	64,000
PPG Industries, Inc.	Corpus Christi, Tex.	27,000

(B) Chromic(VI) Acid - Chromic(VI) acid has been produced at four locations, listed in Table 3, by reacting sodium dichromate with sulfuric acid. The waste solution contains chromium ions. The two operating plants have controls.

Table 3. CHROMIC(VI) ACID PLANTS

Company	Plant Location	Capacity (metric tons/yr)
Allied Chemical Corp.	Baltimore, Md.	
Diamond Shamrock Corp.	Castle Yanes, N.C.	16,000
Essex	Kearny, N.J.	12,000 (standby)
McGean	Cleveland, Ohio	1,800 (standby)

(C) Chrome Pigments - In general, chrome pigments are made by precipitation or crystallization from solution, followed by filtration, drying, and possibly calcining. Waste effluents contain chromium, while stack emissions from dryers and calciners contain particulate chromium compounds. Producing companies are listed in Table 4.

(D) Other Chemicals - The production of other chromium compounds is expected to yield the same types of emissions as the production of chrome pigments. The low production level of these compounds eliminated them from further consideration.

- Electroplating

The major use for chromic(VI) acid is in chrome electroplating. An aqueous solution of the acid is used, resulting in a chromium-contaminated water discharge. Gas evolution during plating also causes the formation of a chromium-containing mist which must be vented to the outside.

There are several thousand electroplating facilities in the U.S.; some are independent plants and some are captive to such activities as automobile manufacture and the production of electrical equipment. Larger operations are generally controlled, but some smaller ones are not.

- Leather Tanning

Most leather goods are tanned with a reduced sodium dichromate solution. Effluents from the process contain chromium ions.

Table 4. CHROME PIGMENT PLANTS

Company	Location	Products
Allied Chemicals Corp.	Marcus Hook, Pa.	Lead chromate
Hercules, Inc.	Glen Falls, N.Y.	Chromium oxide Lead chromate Molybdate orange Zinc chromate Compounded chrome pigments
Kewanee Oil Co.	Louisville, Ky.	Lead chromate
Mineral Pigments Corp.	Beltsville, Md.	Chromium oxide Lead chromate Molybdate orange Zinc chromate
Minnesota Mining & Mfg.	Copley, Ohio	Chromium oxide
Pfizer, Inc.	Lehigh Gap, Pa.	Chromium oxide & hydroxide
Reichold Chemicals, Inc.	Brooklyn, N.Y.	Molybdate orange Zinc chromate Compounded chrome pigments
Richardson-Merrill	Phillipsburg, N.J.	Lead chromate
Rockwood Industries, Inc.	S. Plainfield, N.J.	Chromium oxide
Shepherd Chemical Co.	Cincinnati, Ohio	Chromium oxide & hydroxide

- Metal Treatment, Wood Treatment, and Corrosion Control

  A number of metals and woods are treated with a chromium solution to inhibit corrosion and decay. Recirculating water systems often contain chromium compounds to prevent corrosion. In all cases, the waste discharge will contain chromium in solution.

- Textiles and Dyes

  Certain dyes and pigments employ a chrome mordant. Since the dyeing operation is carried out in a water solution, the water effluent is contaminated with chromium.

References utilized in compiling the analysis presented in Section 2.1 are listed in Table 5.

2.2 RESULTS OF PRESAMPLING SURVEYS AND CHOICE OF SAMPLING SITES

A presurvey effort was scheduled for plants in the following five industrial categories:

- Chrome pigment producers
- Electroplating plants
- Ferrochromium plants
- Leather tanneries
- Sodium dichromate/chromic acid producers

The surveys included determination of the present state of control technology, actual air and water emission points, accessibility of sampling sites, presence of interfering structures, other possible sources of chromium emissions in the area, and the cyclic nature of plant operations. Previous experience has proven that sampling without consideration of these factors can

Table 5. BIBLIOGRAPHY: CHROMIUM EMISSION SOURCES

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1975 Directory of Chemical Producers, Stanford Research Institute, Menlo Park, California, 1975, 1369 pages.

lead to meaningless results.

The five types of operations were included in the survey to study the greatest variety of emissions. Since the sources of chromium emissions encompass dissimilar processes, it was necessary to survey several types of industries to gain a comprehensive understanding of possible problems.

To assess air and soil sampling potential, airports near the plants were contacted for information on prevailing wind direction before the survey visits. Topographic maps of each site were obtained. The local EPA or State Water Control Board was contacted at the site to obtain NPDES permits and previous discharge reports. Compliance schedules for air emissions were obtained from local Agency personnel. The USGS eight-digit STORET number was also obtained in order to assess information from any river monitoring stations.

The following type of information concerning the basic process description was solicited from plant personnel at each plant site:

- emission points - air, water and solid
- solid waste handling practices
- operating cycle (batch, continuous, cyclic) - best times to sample
- abnormal conditions that might affect sampling validity
- heights of air emission points and water discharge locations
- on-site treatment of process effluent or municipal treatment
- expected chromium valence states at each emission point
- fugitive emissions
- other sources of chromium emissions in the area
- age of facilities

Additional information that was obtained by observation at the plant sites included:

- nature of terrain surrounding the plant site especially in the direction of the prevailing wind
- ease of sampling (both air and water)
- receiving water characteristics (terrain, size, flow, accessibility)
- air emissions (heights of stacks, location, color and frequency of observed emissions, wind direction and velocity, plume rise)
- location of community water supply with respect to plant discharges
- presence of interferring structures
- other industries or emission sources nearby

2.2.1 Chrome Pigment Producers

Chrome pigment producers were judged worthy of study since hexavalent chromium compounds are released into both air and water by this industry. Control technology has been installed at most plants because of environmental standards and the more recent threat of carcinogenic activity by lead chromate. However, inorganic pigments are typically produced in particle sizes of 0.1 to 10 um, which are difficult to control. A dryer with uncontrolled emissions of 10 g/kg may still have emissions of 0.5 g/kg after a control device is installed.

An attempt was made to arrange surveys at three plant sites in cooperation with the Dry Color Manufacturers' Association (DCMA). Mr. Gregory Bruxelles,[a] head of the lead chromate subcommittee

[a]Director of Marketing Services, Coatings and Specialty Products Department, Hercules Incorporated, 910 Market Street, Wilmington, Delaware 19899

of the DCMA, was unable to furnish information and suggested that the individual chrome pigment producers should be contacted directly. Based on the variety of compounds made, surveys were conducted at the Mineral Pigments Corp. at Beltsville, Md., and at Hercules, Inc., at Glens Falls, N.Y. Details of the sampling survey visits are presented in Appendices A and B with the sampling and analyses results. The Hercules, Inc. plant was chosen because the effluent discharge at the Beltsville, Md., Mineral Pigments Corp. site was below the water level of a creek tributary and, therefore, somewhat inaccessible for sampling. Eventually, both sites were sampled on request of the Project Officer, Dr. Vincent DeCarlo, when it was learned that the Mineral Pigments factory had come under the scrutiny of the Occupational Safety and Health Administration for alleged violations of Federal Health and safety standards due to work-place emissions of lead compounds. The sampling and analysis efforts at Mineral Pigments included lead in addition to chromium determinations.

3.2.2 Electroplating Plants

Electroplating operations discharge hexavalent chromium into the air and water when uncontrolled. Defoaming agents are commonly used to suppress the formation of chromic(VI) acid mist emissions, while larger facilities also employ scrubbers. Water treatment is not as extensive, and smaller operations may discharge untreated wastes to the municipal water system.

Since plating plants number in the thousands, 13 sites in the Dayton, Ohio area were considered. Miller Plating Company and the Stolle Corporation were surveyed as potential sampling sites. The Stolle Corporation was selected based upon the accessibility of sampling locations and the fact that it is located within 0.5 km of the Dayton Laboratory of MRC. The results of the sampling and analysis effort at the Stolle Corp. facility are presented in Appendix C.

2.2.1 Ferrochromium Plants

Producers of ferrochromium were selected for presampling survey in the metallurgical industry because the chromium content in their emissions is higher than in related areas such as stainless steel production. The ferrochromium plant sites surveyed included the Chromium Mining and Smelting Corporation (Chromasco) at Woodstock, Tennessee and the Interlake, Inc. plant at Beverly, Ohio.

The Chromasco site was surveyed on September 1, 1976 but no visit could be arranged with plant personnel. Discussions with Shelby County (Tennessee) Health Department personnel responsible for air and stream pollution and a visual survey of the plant site indicated no potential problems in sampling.

The Interlake, Inc. plant at Beverly, Ohio was not selected for sampling for three reasons: (1) their present process precludes the possibility of chromium-bearing wastewater, (2) highly efficient baghouse particulate controls minimize the probability of significant air emissions, and (3) the plant site is located about 0.8 km from a 1400 MW coal-burning power plant. The Interlake site is completely surrounded by the power plant property, with its ash beds, ponds, and chrome ore and slag piles, which would have invalidated soil measurements for chromium.

2.2.4 Leather Tanneries

There are some 500 leather tanneries in the U.S., and a number of the larger ones are given in Table 6 (1). The greatest concentration occurs in Essex County, Mass. (see Figure 2). Pre-sampling survey visits were conducted at the H. J. Hidden Tannery in North Adams, Mass. and the Saco Tanning Co. in Saco, Maine. Either of these sites would have qualified for sampling chromium, but the Bresnor Tanning Company in Penacook, New Hampshire was selected since its water effluent is treated at a local municipal sewage treatment plant. This relationship furnished the opportunity of sampling tannery effluent before and after treatment. The survey reports for the tannery and the treatment plant are presented in Appendices D and E of this report.

2.2.5 Sodium Dichromate/Chromic(VI) Acid Producers

At the present time, only three companies are actively manufacturing these chemicals (Tables 2 and 3). Visits were made to the Allied Chemical Corp. site in Baltimore, Md. and the Diamond Shamrock Corp. plant in Castle Haynes, N.C. The Allied site was found to be unsuitable for sampling for three reasons: (1) the plant is located in a highly industrialized and commercial area just north of the Northwest Harbor of Chesapeake Bay, (2) the potential for downwind air sampling is hampered by the prevailing wind which is from the northwest to the harbor, and (3) collection of soil samples is impossible due to the urban nature of the area. The Diamond Shamrock facility opened in 1972 and is equipped with the latest pollution control technology. All hot flue gases pass through two electrostatic precipitators (99.8% efficient).

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(1) "Thomas Register, 1975" Thomas Publishing Co., New York, N.Y., 1975, pp 8787-8788.

Table 6. SELECTED LARGE TANNING FACILITIES AND LOCATIONS[1]

Arizona

[illegible] Hide Co. – Phoenix

Illinois

[illegible] Tanning Co. – Chicago
[illegible] Rawhide Mfg. Co. – Chicago

Iowa

Spencer Packs Inc. – Spencer

Maine

[illegible] Tanning Co., Inc. – East Milton

Massachusetts

Beacon, Inc. – Beverly
A. M.Chandler & Sons, Inc. – Boston
[illegible] Leather Co., Inc. – Danvers
Hyde and Morrison Tanning Corp. – Haverhill
Moose Leather Co. – Millbrook
Nob-Hill Leather Co., Inc. – Peabody
Peerless Leather Co., Inc. – Peabody
[illegible] Leather Co., Inc. – Peabody
S. S. Pierce Leather Co., – Peabody
Robbins Leather & Finishing Co. – Peabody
Sun Tanning Corp. – Peabody
Sachsenmaier Tanneries, Inc. – Salem
Warren Tanning Co., Inc. – Salem
[illegible] Tanning Co. – Taunton
Arnold Bros. Tanning Corp. – Woburn
Berwig Bros. Tanning Co., Inc. – Woburn

New Jersey

A. J. Am. J. C. Pilar, Inc. – Newark

New York

Berwyn Page Corp. – Dresden
[illegible] Tanning Co. – Gloversville
Leather Group Inc. – Gloversville
Liberty Tanning Corp. – Gloversville
Eastern Tanning Co., Inc. – New York
Milton Hochhauser Leather Co., Inc. – New York
Marshall Leather Finishing Co., Inc. – New York

Oregon

Muir and McDonald Co. – McCoy

Pennsylvania

Wm. C. Brown Leather Co. – Philadelphia

Texas

Wolfson and Sons, Inc. – San Antonio

Utah

Wills Tannery, Inc. – North Salt Lake
J. S. Dorfflinger and Associates – Tooele

Wisconsin

[illegible] Tanning Corp. – Milwaukee
Wright Tanning Co. – Milwaukee
Anton Corp. – Sheboygan
Wilmot Tanning Co. – South Milwaukee

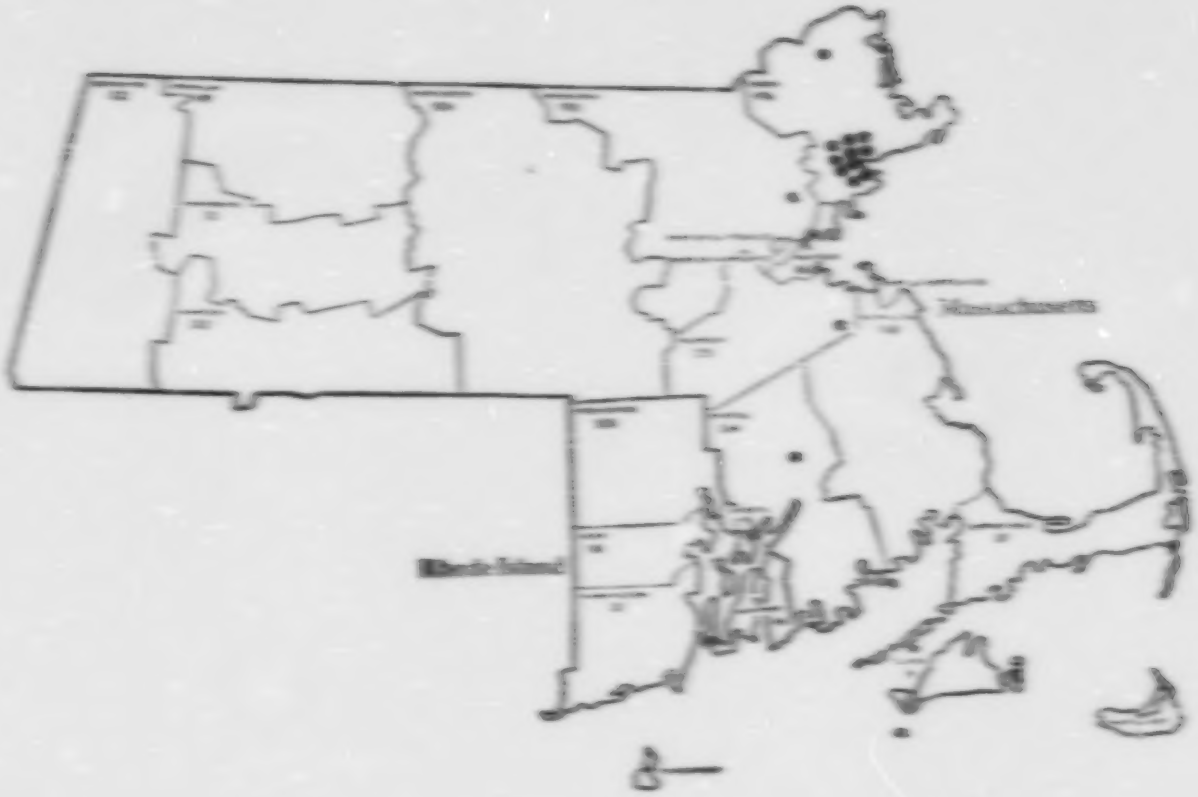

Figure 2. Location of Leather Tanneries in Essex County, Massachusetts.

Wastewaters and waste muds are treated to convert chromium(VI) into an insoluble chromium(III) compound which settles out in treatment lagoons. A complex monitoring system samples ambient air in all directions around the plant and tests the water effluent. It was judged that chromium measurements at this modern and well-controlled complex would not be representative of the industry.

2.3 FINAL SELECTION OF SAMPLING SITES

As a result of the surveys, sampling and analysis of chromium was conducted at the four industrial sites and the two sewage treatment plants listed in Table 7. The second sewage treatment plant, not mentioned previously, is located on Guthrie Road in Dayton, Ohio about 1.6 km from MRC's Dayton Laboratory and is adjacent to the Stolle Corporation electroplating operation. Although this treatment plant does not handle the Stolle Corporation wastewater, City of Dayton Water Department personnel stated that the bulk of chromium they receive comes from chromium plating operations in the area.

Table 7. LIST OF FINAL SAMPLING SITES BY INDUSTRIAL CATEGORY

Sampling Site	Location	Report Appendix
Chrome Pigments		
Mineral Pigments Corp.	Beltsville, Md.	A
Hercules, Inc.	Glens Falls, N.Y.	B
Electroplating Plants		
The Stolle Corp.	Dayton, Ohio	C
Leather Tanneries		
Spencer Tanning Co.	Penacook, N.H.	D
Sewage Treatment Plants		
Penacook Sewage Treatment Plant	Penacook, N.H.	E
Guthrie Road Sewage Treatment Plant	Dayton, Ohio	F

3. SAMPLING SITES

3.1 AIR SAMPLING SITES

Diffusion models of the two chrome pigment plants and the electroplating plant were developed based on the emission rates and the effective heights of emissions as given by plant operating management or estimated by MRC personnel. The Gaussian plume model as developed by Martin and Tikvart (4) employs annual joint frequency distributions of atmospheric stability, and wind speed and direction as obtained from the National Climatic Center in Asheville, North Carolina. These data were employed as input into MRC's computer program to calculate relative concentration or dosage isopleths surrounding each plant site of interest. The listings from this program are presented in Table 8. This procedure has been well documented by the EPA in their descriptions of the Climatological Dispersion Model (CDM) (5). The result of the modeling effort was a definition of potential chromium contents in air surrounding the plant sites based primarily on the point source emissions defined in the surveys. This result did not, however, account for fugitive

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(4) Martin, D. O. and J. A. Tikvart, "A General Atmospheric Diffusion Model for Estimating the Effects on Air Quality of One or More Sources," presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minnesota, June 23-27, 1968, 18 pp.

(5) Busse, A. D. and J. R. Zimmerman, "User's Guide for the Climatological Dispersion Model" EPA-R4-73-024 U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, December 1973.

Table 8. LISTINGS FOR AIR DIFFUSION COMPUTER MODEL

```
C       M-1 DIFFUSION PROGRAM
C       REVISED 9/10/76 - LO MOTE
C
      DIMENSION SHOT(101,SVET(101,HST(101,GSOT(101,ST(101,WT(101
      DIMENSION SC(6,16,6),A(101,B(101,C(101,WSA(6)
      DIMENSION RHOR(1801,RVER(1801,VAL(1801,ACCUR(180)
      DATA A,B,C,WSA/.00004,.095,.819,1.06,6.758,16.05,.0015,.088,.119,
     1.092,.011,.084,.192,.186,.110,.079,.063,.048,0.006,1.098,.911,
     2.916,.809,.180,1.941,1.149,.911,.705,.678,.74,.986,.922,.905,
     3.881,.871,.814,-9.8,0,0,-10,-34,-46,0,0.27,0.3,0,-1.7,-1.8,
     4.,.55,6e0,.,67,0,95,0,97,0,98,0,81,10,80/
      LUN=1
      LUW=6
      READ(LUR,174) DELTAR,RADRAD                                        091076
      READ(LUR,76) IRAD,ESTART,T
      READ(LUR,76) GRID,ALWT,DM
      READ(LUR,81 ((SC(M,N,J),J=1,6),N=1,6),M=1,6)
      READ(LUR,106) (SHOT(IL),SVE(IL),HST(IL),GSOT(IL),ST(IL),WT(IL),
     1IL=1,150R)
      WRITE(LUW,916) GRID,ALWT,DM,150R,IREC,R,IUR
      DO 19 IQ1,150R
      WRITE(LUW,915) SHOT(I),SVET(I),HST(I),GSOT(I),ST(I),WT(I)
   19 CONTINUE
      CALL.19159/100,
  716 IRAD=IRAD+DELTAR
      RAD=IRAD/1000,
      WRITE(LUW,781)
      IF(IRAD-RADRAD)720,720,799
  720 C=0
      DO 748 IANG=1,360,6
      K=K+1
      ANGLE=C*IANG
      RHOR(K)=ESTART+RAD*SIN(ANGLE)
      RVER(K)=TSTART+RAD*COS(ANGLE)
  748 CONTINUE
 1500 DO 1110 M=1,IREC
 1110 ACCUR(M)=0.0
      DO 97 IL=1,150R
      IPT=1
      SHOR=SHOT(IL)*WT(IL)/(DRUN10)
      SVER=SVET(IL)*WT(IL)/(DRUN10)
      USHST(IL)
      GSOSGOT(IL)
      C=GT(IL)
      W=WT(IL)
      IF(W-25) 500,501,501
  501 IPT=0
  500 DO 110 M=1,IREC
      VAL(M)=0.0
      DO 98 N=1,10
      DRUN
      RAD=(RR-1.)*100.0927
      SIN=SIN(RAD)
      COS=COS(RAD)
      RCOR=(RVER-RVER(M))*COS+(SHOR-RHOR(M))*SIN
      DRUN=W/.894
   15 DO 101 I=101,IPT
   17 IF(I) 98,96,15
   18 IF(I-W/2.) 98,98,19
    9 VAL(M)=SHOR(I)*(SVER-RVER(M))*SIN-(SHOR-RHOR(M))*COS(I)
```

```
      [[[=.999[4
      IF(CK-Y) 96,96,66
   66 ARG2=(CK-Y)/CK
      GO TO([3,[85],[PT
  [85 Y=(W/2.)+ADV(6PI) 100,100,6P85
  100 IF(W-.8986*PI 15,15,105
 1005 GO[.196*PI*X=0.049W[000]/W**2
      GPO,707[*WP=W/0.1
      ##0,0##P
 1007 IF(Y-(W/2.)) 181,181,99
  105 GO[.895*Y-W[/W
      WPRGORT((-P**PI+(W=W/9))
      ###,0#P
  105 IF(Y-(W/2.+.595[0)) 181,181,99
   10 GO[
  181 DO 98 LOUK=1,7
      GO TO(1810,1811),IUR
 1810 GO TO(502,503,504,505,506,507,90[,LOOK
 1811 GO TO([50,[60,[70,507,508,509,5701,LOOK
  502 DM=1.*#0DM[S
      FREQ=1.0
      L01
      GO TO 97
  503 DM=DM[S
      FREQ=1.0
      L02
      GO TO 97
  504 DM=DM[S
      FREQ=1.0
      L03
      GO TO 97
  505 DM=[[[[[.
      FREQ=1.0
      L04
      GO TO 97
  506 DM=[DM[S*[00.01/9.0
      FREQ=0.00
      L04
      GO TO 97
  507 DM=DM[S
      FREQ=0.6
      L04
      GO TO 97
  508 DM=DM[S/9.0
      FREQ=0.5
      L04
      GO TO 97
  509 FREQ=1.0
      DM=DM[S
      L05
      GO TO 97
  570 FREQ=1.0
      DM=DM[S
      L05
   97 [###1
      GO 99 J=1,6
      L###
      IF(###-01 ####,####,####
 9003 GO TO(2024,2025),IUR
 9002 FORC[###,N,J)
```

```
      GO TO 8888
8888  FORMAT(5H1,J1+5E16.4,J)
2005  IF(F) 99,99,10
   10 WRITE(A,J)
      DO 70(20,8881),IUR
   99 IF(LOOP-91 881,2010,8810
8810  LOG
  881 CCAL
      HOHS+80(1),N=0,1ECC(981/WB
8410  IF(H-OM) 84,84,99
   84 IF(XP-1000,) 88,81,85
   88 IF(XP-100,) 828,881,881
  198 LOL=10
      GO TO 81
  881 LOL=8
   81 GO TO(881,811),IUR
  827 IF(H-80.) 810,810,811
  810 SIG1=80.0=H
      IF(SIG1-80,) 881,881,8101
8181  SIG1=80,
      GO TO 881
  811 SIG1=0.0
  881 SIGZ=SQRT((AIL(ARG1(EP(-SIG1**2/(LL(LL(((*SIG1**2
   88 ARG1=1-0,8888(1)/(SIGZ*SIG1*Z)
      IF(ABS(ARG1)-60.0) 87,99,99
   87 GO TO(871,871),IUR
  871 IF(SIGZ-0,0700) 87,87,86
   87 LL=1
      8048
   86 C1=(PRESS,888*8P*ARGS*EXP(ARG1)/(SIGZ*W*8*8)
      GO TO(48,841),LL
   48 CALL
      GO TO 998
   84 DUM1=1,870(M1888-8181888
9991  DUM=SQRT(DUM1)-C(L)
9998  DUM=ALOG(DUM)/A(L)
      WRITE(IOUT,DUM)/A(L)
   91 IF(81-1000,) 88,88,89
   88 IF(81-100,) 881,881,888
  881 LOC(10
      GO TO 883
  888 LOC=10
  885 DUM1=(,870(M1888-8181888
9998  DUM=SQRT(DUM1)-C(L)
9994  DUM=ALOG(DUM)/A(L)
      WRITE(IOUT,DUM)/A(L)
   80 IF(XP-8,8818) 84,88,88
   88 8888
      LOG1
   87 C2=(8,88*PRESS*8P*ARG81/(DM*W*8*8)
      GO TO(85,881),LM
   85 CALL
      GO TO 998
   84 8888,8881(8)/,888
      LOG2
      GO TO 87
   82 A0=81(8)/,888
      LL=2
      SIGZ=0,87(M
      ARG1=(,888HOH1/(8818*8818*8)
```

```
      GO TO 88
   81 CSNCL=((ISP-NS1/IRS1)*0.5)+1.0
  990 CSNCB=EXP(-(ISP/NB1/3600.))
      ROTOT=EXP(-(ISP/NB1/3600.))
  992 VAL(M)=VAL(M)*CSNCB+ALMT
   99 CONTINUE
   98 CONTINUE
   96 CONTINUE
      ACCUM(M)=ACCUM(M)+VAL(M)
  110 CONTINUE
   97 CONTINUE
      WRITE(LUN,104)
      WRITE(LUN,108)
      WRITE(LUN,110) IRAD
      DO 11018 ASI,IREC
      RHOOM=1
11018 WRITE(LUN,108) R,RHOR(M),AVER(M),ACCUM(M)
      GO TO 710
  199 CONTINUE
      CALL EXIT
    1 FORMAT(1H1)
    2 FORMAT(7E12.6)
   76 FORMAT(F5.1,F7.0,F6.0,6I8)
   75 FORMAT(8X,8E12.5)
  104 FORMAT(1H0,3X,'COORDINATES   VALUE IN G/M**3')
  108 FORMAT(1H ,1X,F10.3,F8.1,F8.1,F12.6)
  106 FORMAT(1H ,6F9.1,F6.0,F6.0,3X,F10.6,F10.5)
  107 FORMAT(1X,6F9.1)
  108 FORMAT(1H0,3X,'SUBSUMRATION')
  109 FORMAT(1H0,F10.7,F10.5)
  110 FORMAT(1H ,'  RADIUS = ',I5)
  175 FORMAT(F5.0,3X,I5)
  810 FORMAT(1H0,'DRID = ',F10.5,'ALMT = ',F10.5,'OMEG = ',F10.5,
     1'IBUR = ',I5,'IREC = ',I5,'IS = ',I5,'IUR = ',I5/
  815 FORMAT(1H0,'ROT = ',F10.5,'AVET = ',F10.5,'MT = ',F10.5,
     1'ROT = ',F10.5,'GT = ',F10.5)
  710 FORMAT(1H1)
      END
```

emission points. For this reason, perimeter air sampling was conducted at each plant site where air emissions were suspected.

The ambient air sampling arrangement employed is presented in Figure 3. A portable meteorological station was used to determine wind speed and direction. The logic chart shown in Figure 4 was employed to estimate atmospheric stability class. One 24-hour sample was obtained at each of the three plant sites mentioned previously, employing a minimum of six high-volume samplers. The results permit calculation of each plant's chromium emission rates, including both point and fugitive source contributions. Where no inorganic air emissions were suspected, such as the tannery and sewage treatment plants, high-volume samplers were not employed.

The tannery and the two sewage treatment plants were sampled to determine "organic" chromium species in air. Here "organic" chromium is used to mean any chromium compound which is volatile or has affinity for nonpolar organic resins used to concentrate materials from water or air. These would include chromium organic compounds such as complexes of chromium with organic ligands.

These types of chromium compounds are known to exist and if they occur in nature they would be expected in tannery waste or sewage since these media contain a wide variety of organic substances and support biological activity. For example, see the work of Toepfer, et al. (6) on chromium in yeast extracts.

(6) Toepfer, E. W.; W. Mertz, M. M. Polansky, E. E. Roginski, and W. R. Wolf, "Preparation of Chromium-Containing Material of Glucose Tolerance Factor Activity from Brewer's Yeast Extracts and by Synthesis," Journal of Agricultural and Food Chemistry 25, 162-166 (1977).

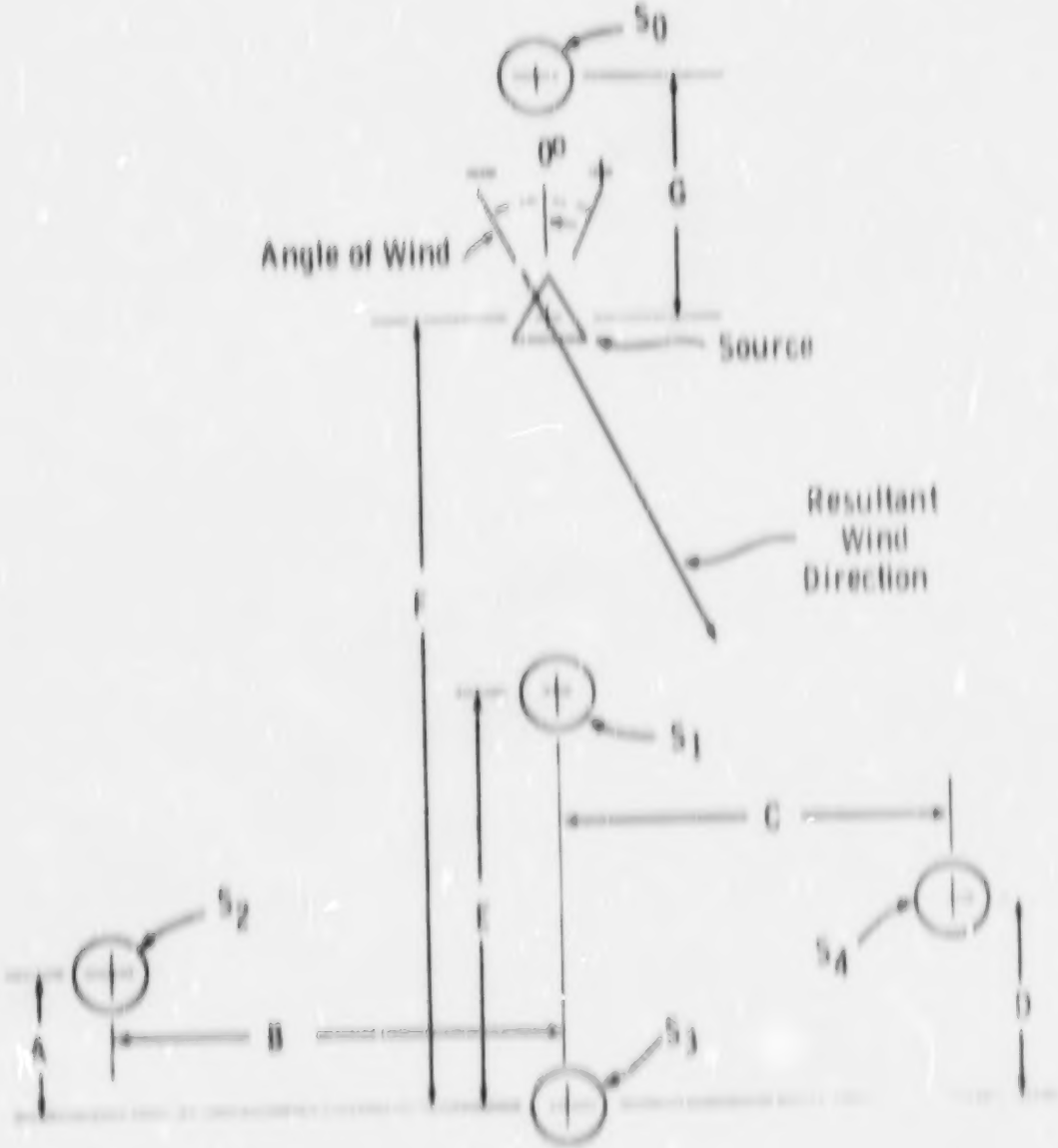


Figure 3. Ambient Air Sampling Arrangement.

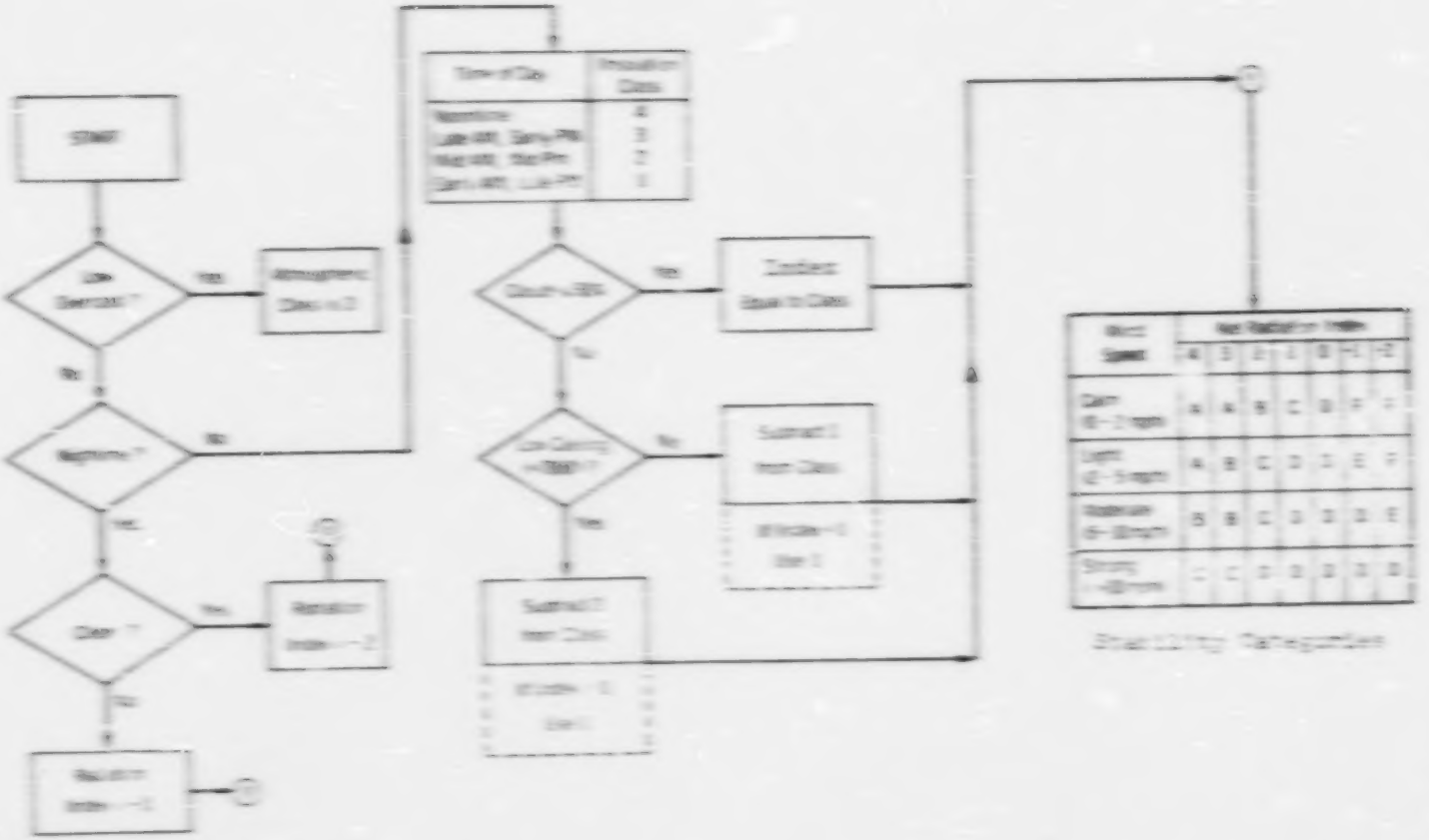


Figure 4. Flow Chart of Atmospheric Stability Class Determination.

3.2 WATER SAMPLING SITES

Water sampling sites varied from plant to plant depending upon the body of water into which the plant effluent was discharged. A 24-hour composite sample was taken at the outfall of each plant. If the plant was discharged into a stream, one sample was taken above the outfall, one at the outfall, and two at locations at staggered intervals downstream of the outfall.

Sediment samples in bodies of water were obtained where possible to determine chromium accumulation. These samples were taken in the same locations as the water samples. One sample above the outfall and two at staggered locations below the outfall were collected.

The specific sampling sites could only be determined as a result of the survey visits. These sites for each plant are described in the respective appendices.

The technology required to examine water or other media for ionic (e.g., nonvolatile) chromium organic compounds does not exist at present. It is believed that liquid chromatography with on- or off-line atomic absorption detection would be needed to study these systems in detail.

3.3 SOIL SAMPLING SITES

The soil sampling sites were selected based on the seasonal concentration isopleths developed employing the Gaussian plume model. The computer program employed at MRC is capable of locating points of maximum ground level concentration based on the point-source data. Five samples were obtained at each plant. Since the diffusion model predicted an area of maximum

concentration and a secondary maximum concentration area, two samples were taken in each of these areas (one close to the plant boundaries and one farther away from the plant). The fifth sample was taken as a background sample upwind of the facility. Duplicate samples were obtained at each sample site.

4. SAMPLING METHODS AND EQUIPMENT

4.1 AIR SAMPLING

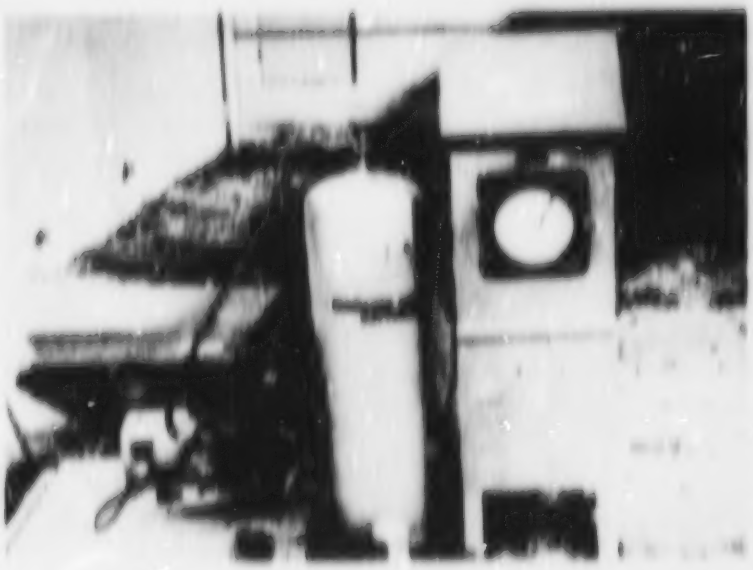
High-volume samplers[a] were used to collect particulates from ambient air. These samplers have automatic flow controllers that adjust the flow to a precalibrated flow setting. In this case, 0.019 m^3/s (40 cfm) was the flow rate used.

Sampling was conducted over a 24-hour period for perimeter samples and for 4-6 hours using the downwind array. The particulate was collected on 20.3 cm x 25.4 cm Millipore® filters. These filters exhibit a chromium content of 0.002 ug Cr/cm^2.

At the start of the program, small gasoline-powered generators were employed to permit sampler operation in remote areas. Later in the program the gasoline-powered generators were converted to propane by employing liquid propane-gas carburetion kits. Liquid propane-gas vapor withdrawal tanks containing sixty pounds of fuel permitted 50 hours of continuous, unattended high-volume sampler running time. Flow controllers (Accu-Vol Controller Model GMW-310) were employed to ensure a constant sampling flow rate independent of voltage variation, temperature or pressure changes and filter loading. The high volume sampler arrangement employing the propane fuel generator is shown in Figure 5.

---

[a]General Metal Works, Inc., 8368 Bridgetown Road, Cleves, Ohio 45002.



'igure 5. High-Volume Sampler with Propane Fuel Generator.

Air samples were also obtained at some locations for organic chromium species. These samples were taken using the sampling train shown in Figure 6. Ambient air was pumped through a glass fiber filter and an XAD-2 resin tube at between 230 cm^3/s and 330 cm^3/s over a period of four hours. The volume of gas sampled in each run was measured by a dry test meter. After sampling, the resin tubes were capped at either end for transport back to the laboratory.

4.2 WATER SAMPLING

The water sampling methods and equipment employed depended on the plant location, process operation, and characteristics of the body of water to be sampled. However, some basic methodology was established which could be used in the various sampling situations.

Two types of commercial water samplers were used. These were the Manning water sampler[a] and the ISCO water sampler[b]. Both samplers are capable of taking sequential and composite samples either on a time or flow proportional basis. Since these units are battery powered, they are useful for sampling in remote locations.

[a]Manning Environmental Corp., 120 DuBois Street, P. O. Box 1356, Santa Cruz, California 95061.

[b]Instrumentation Specialties Company (ISCO), P.O. Box 5347, 4700 Superior Street, Lincoln, Nebraska 68505.

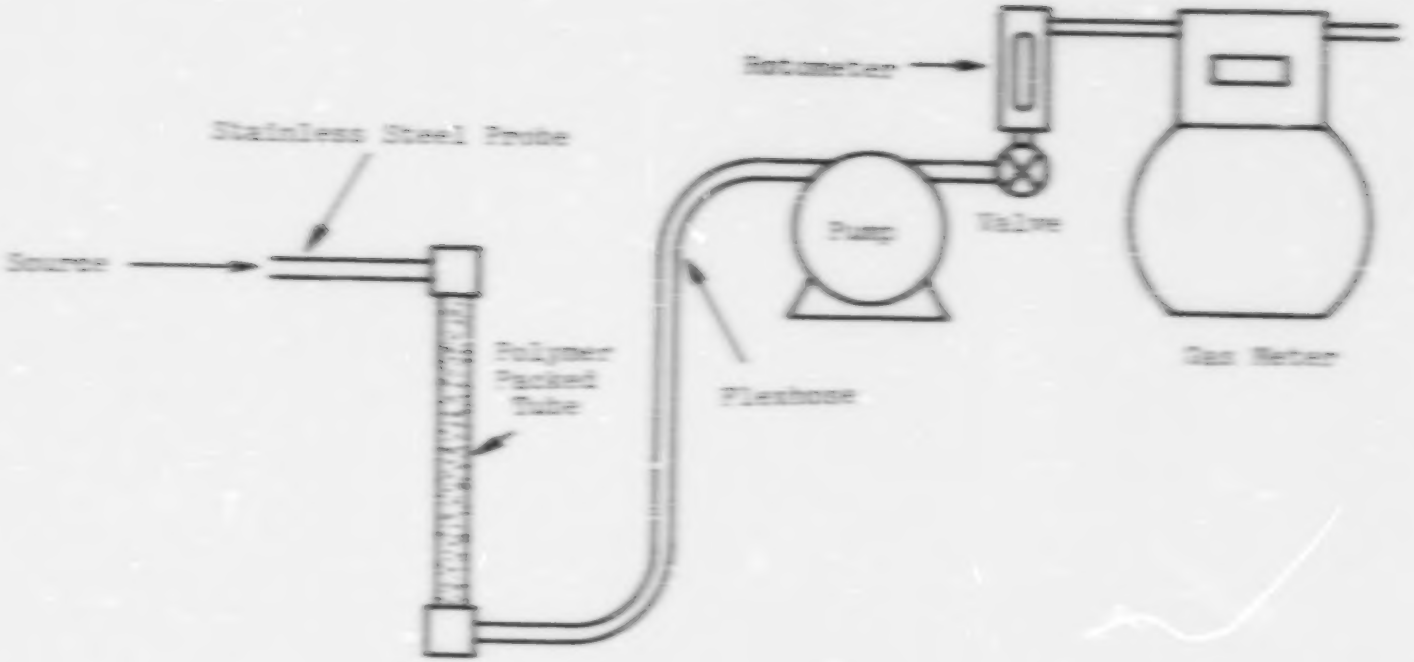


Figure 1. Porous Polymer Vapor Sampling Method.

Another type of water sampler employed was designed by MRC to fit in a Sears-Roebuck Craftsman toolbox (45.7 cm x 22.9 cm x 20.3 cm). The apparatus consisted of a variable speed peristaltic pump fitted with a Masterflux model 7016 pump head powered by a 12-volt motorcycle battery. The pump speed was set so that a 4-liter polyethylene Cubitainer® was filled over a 24-hour sampling period. Two views of the "toolbox" sampler are presented in Figure 7.

Each water sample taken exceeded the required volume of approximately 3 liters. The samples were filtered through an 0.45-micron Millipore® filter in the field to separate soluble and suspended particles. It was preserved by adjusting the pH of the sample to 1.5-5.0 using a field-determined amount of 6M HNO_3/3M H_3PO_4.

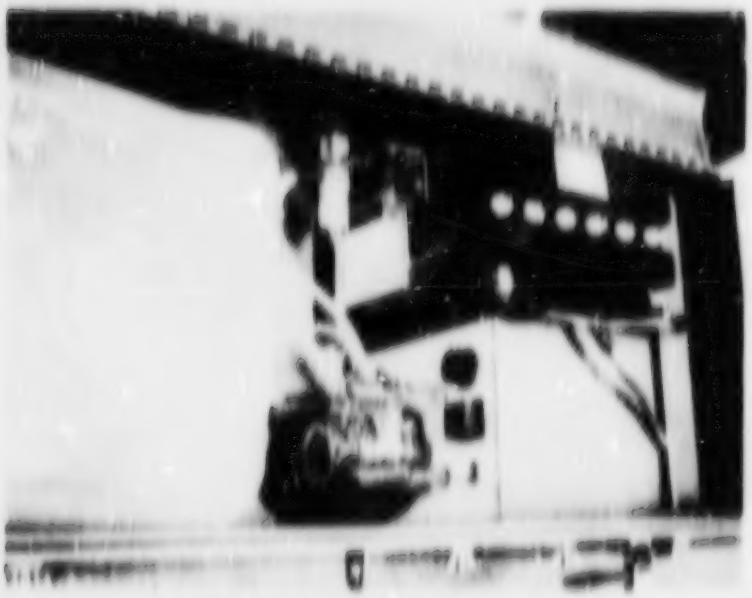
Water samples for "organic" chromium species were obtained at one location. They were pumped through an XAD-4 resin tube at a rate of 200 ml/min using a variable speed peristaltic pump. Approximately 8 liters of sample were pumped through each tube. Approximately 500 ml of 0.1M HCl was then pumped through each tube to rinse "inorganics" that may have been left on the resin. The tubes were then sealed at the ends for transport back to the lab.

4.3 SOIL, SEDIMENT, AND SLUDGE SAMPLING

Soil samples were obtained using a core-sampling device. Cores 5.3 cm in diameter and 7.6 cm deep were collected and placed in plastic bags.

Sediment samples were taken by scooping sediment off the bottom of the body of water being sampled. Sludge samples were taken in much the same manner. These samples were placed in polyethylene jars for transport to the laboratory.

(a) External View of "Toolbox" Sampler.



(b) Internal View of "Toolbox" Sampler.

Figure 7. Photographs of "Toolbox" Sampler.

5. SAMPLE ANALYSIS PROCEDURES

5.1 ANALYSIS OF AIR PARTICULATE SAMPLES

Immediately upon completion of the air sampling, the tared filter (20.3 cm x 25.4 cm Gelman[a] spectroquality glass fiber filter) on which air contaminants were collected was placed between onionskin paper and transported back to the laboratory in a sealed envelope. Upon arrival at the laboratory the filters were removed from the envelope, desiccated for 24 hr, and the mass of particulate loading determined. After the unexposed portion of the filter had been carefully trimmed, the exposed portion was analyzed.

A segment of the filter (~5.7 cm x 18 cm) was acid extracted according to the procedure described in Section 5.5. Chromium(VI) analysis was performed using the ADPC/MIBK extraction procedure described in Section 5.6.

Recovery studies were undertaken to verify the acid extraction-analysis methodology. Portions of Gelman spectroquality glass filters were spiked with standard solutions of chromium(VI) or chromium(III), dried, and processed through the low temperature ash-acid extraction scheme (Section 5.5). Analyses were carried out on the Varian AA-6 atomic absorption instrument as described in Section 5.7. The results are presented in Table 9.

---

[a]Gelman Instrument Company, P. O. Box 1448, Ann Arbor, Michigan 48106.
[b]Parr Instrument Company, 211 Fifty-Third Street, Moline, Illinois 61265.

Table 9. RECOVERY OF CHROMIUM(VI) AND CHROMIUM(III) SPIKED FROM HIGH-VOLUME FILTERS

Sample	Spike	Total Cr % Recovery	Percent Recovery by Species
1	1.00 mg Cr(VI)	103.1	6.5
2	1.00 mg Cr(VI)	104.1	1.9
3	1.00 mg Cr(VI)	104.5	26.4
4	1.00 mg Cr(VI)	103.1	9.1
	Avg. total chromium recovery = 103.7 ± 0.7%		
5	0.500 mg Cr(III)	95.4	95.4
6	0.500 mg Cr(III)	96.0	96.0
7	0.500 mg Cr(III)	97.1	97.1
8	0.500 mg Cr(III)	95.4	95.4
	Avg. total chromium recovery = 96.0 ±0.8%		
	Avg. chromium recovery = 96.0 ± 0.8%		

These data indicate that while the recovery of total chromium, regardless of species, is excellent, the recovery of chromium(VI) through the extraction scheme is low and highly variable; therefore, the only reliable air sample data are those for total chromium. Chromium (VI) data should be regarded only as an indication as to whether hexavalent chromium was present in the original sample.

Chromium(VI) is the highest oxidation state of chromium. When chromium(VI) oxide is dissolved in water, dichromate ($Cr_2O_7^{2-}$) is formed at low pH and chromate (CrO_4^{2-}) is formed at high pH (7). Dichromate is a powerful oxidizing agent

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7\,H_2O \quad E^\circ = 1.33v$$

which readily oxidizes organic matter in water, soils and sediments (8). Chromate is a less powerful oxidizing agent.

$$CrO_4^{2-} + 4H_2O + 3e^- \longrightarrow Cr(OH)_3(s) + 5OH^- \quad E^\circ = 0.13v$$

Thus, chromium(VI) should not persist in any medium containing organic matter at low pH, but it might be stable in natural matrices at high pH (9). Apparently, there is enough organic material or other oxidizable material available during the acid extraction procedure to allow partial conversion of chromium(VI) to chromium(III).

5.2 ANALYSIS OF SOIL, SEDIMENT, AND SLUDGE SAMPLES

Soil, sediment and sludge samples were transported back to the laboratory in appropriately labeled plastic sampling bags or acid-cleaned (1:1 HNO_3), wide-mouth polyethylene bottles. Upon arrival at the Dayton Laboratory each sample was removed from its container and carefully mixed to insure homogeneity. Inorganic and organic matter larger than ~2 mm was removed, and the sample was placed in an acid-cleaned (1:1 HNO_3), 100 mm x 80 mm Pyrex storage jar, and air dried for 48 hours.

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(7) Cotton, F. A. and G. Wilkinson, "Advanced Inorganic Chemistry," Wiley-Interscience, New York, N.Y., 1966, pp 828-829.

(8) "APHA, Standard Methods for the Examination of Water and Wastewater," 13th Ed., American Public Health Association, Washington, D.C., 1971, pp 495-499.

(9) Pankow, J. F., D. F. Leta, J. W. Lin, S. E. Ohl, W. F. Shum and G. E. Janauer, "Analysis for Chromium Traces in the Aquatic Ecosystem," The Science of the Total Environment 1, 17-26 (1977).

A portion of the sample was acid extracted (Section 5.5). Total chromium was determined directly by atomic absorption spectroscopy (Section 5.7). Much difficulty was encountered when the APDC/MIBK extraction procedure (Section 5.6) for chromium(VI) was attempted on the soil extracts. The extremely high iron matrix that resulted from the acid extraction made the pH adjustment step in the MIBK extraction procedure impossible to perform without precipitation of iron hydroxide. Initial precipitation of the iron occurred at a pH between 1.5 and 2.0. APDC quantitatively chelates and extracts iron(III) into MIBK at almost the same pH as employed in the extraction procedure. Even if the precipitation of iron hydroxide could be overcome, the large excess of iron in the sample extract would tie up the majority of the APDC chelate and thus prevent quantitation extraction of chromium(VI) into the ketone layer.

In order to overcome this problem an alternate chromium(VI) separation procedure was developed using a 15 cm x 2 cm Dowex 50W-x8 cation exchange column (Na^+ form). At the low pH of the sample extract, part of the chromium(VI) would oxidise the cation exchange resin. The chromium(VI), in turn, would be reduced to chromium(III) which would be retained by the column. If the acid extract was first partially neutralised to a pH of 1.0 to 1.5, chromium(VI) would pass through the column (see Table 10), iron, chromium(III) and other cations present in the same extract are retained on the column while chromium(VI), present in solution in the anionic forms, passes through the column.

Table 10. RECOVERY OF 0.2 mg OF CHROMIUM(VI) THROUGH A CATION EXCHANGE COLUMN AS A FUNCTION OF pH

pH	Percent Recovery
0.04	89.8
0.01	91.3
0.50	92.1
0.54	91.7
0.98	96.8
1.09	98.4
1.06	96.8
1.48	102.0
1.43	98.2
1.95	101.0

To verify the separation of chromium(VI) by the cation exchange procedure, exactly 10.00 ml of Hercules soil extract and 10.00 ml of the same extract plus a 1.00-mg spike of chromium(VI) were first partially neutralized to a pH of 1.0 to 1.5 and passed through the cation exchange column at a flow rate of about 4 ml/min. Three bed volumes of distilled water followed the sample through the column to ensure quantitative elution into an acid-cleaned 100.0-ml volumetric flask. Table 11 summarizes the recoveries observed for this separation technique.

Table 11. RECOVERY OF CHROMIUM(VI) ION EXCHANGE SEPARATION PROCEDURE

Sample	[Chromium(VI)] in Column Effluent (mg/l)	Percent Recovery
Site 5, sample 1	0.21	
Site 5, sample 1 plus spike	9.79	95.8
Site 5, sample 2	2.73	
Site 5, sample 2 plus spike	12.5	97.7
Site 4, sample 1	0.09	
Site 4, sample 1 plus spike	10.0	99.9
Site 4, sample 2	0.36	
Site 4, sample 2 plus spike	10.33	98.6
	Average Recovery = 98.0 ± 1.[illegible]	

Once the ion exchange separation procedure had been verified, recovery of chromium species through the acid extraction scheme (Section 5.5) was determined. Six soil samples, of about 5 g each, were spiked with chromium(VI) and chromium(III), four with 1.0 mg of chromium(VI), and two with 1.5 mg of chromium(III). The samples were dried, low temperature ashed, digested for 3 hours with HCl and HNO_3, filtered, reduced in volume to ~50 ml, and diluted to 100 ml. A 10-ml aliquot was ion exchanged, then the effluent was diluted to 100 ml and analyzed by atomic absorption. The results are shown in Table 12.

Table 12. RECOVERY OF CHROMIUM(VI) AND CHROMIUM(III) SPIKES FOR SOIL SAMPLE

Sample	Spike	Percent Total Chromium Recovery	Percent Recovery by Species
1	1.00 mg Cr(VI)	89.0	·1
2	1.00 mg Cr(VI)	112.3	·1
3	1.00 mg Cr(VI)	84.0	·1
4	1.00 mg Cr(VI)	121.0	·1
	Average = 102.0 ± 17		
5	1.5 mg Cr(III)	104.0	104.0
6	1.5 mg Cr(III)	107.0	107.0
	Average = 105.5 ± 1.0		

The data indicate that total chromium recovery is good by the procedure; however, the chromium(VI) species is not recovered. As was shown earlier, the chromium(VI) form is not altered during the ion exchange step. It must be concluded that the procedure does result in good total chromium recovery from soil. However, as with the high-volume filters, the determination of chromium(VI) is unreliable. As a consequence, the analysis of chromium(VI) in soil samples was abandoned.

5.3 ANALYSIS OF WATER SAMPLES

Prior to sampling, all glassware and polyethylene sample bottles were rinsed with 1:1 H_2SO_4/HNO_3 or 1:1 HNO_3 before use. As soon as possible upon completion of sampling the water samples were pressure filtered through back-to-back tared 0.45-μm Millipore® filters. The volume of sample passed through each filter was measured. The filtrate was stored in the original sample container which had been thoroughly rinsed, first with distilled water and then with filtrate. The filtered sample was then acidified to a pH of 3.5-5.0 with 6M HNO_3/3M H_3PO_4. The suspended particulate sample was carefully removed from the Millipore® filtration apparatus and placed in a clean plastic petri dish for storage until analysis.

Analysis of the water sample for total chromium was performed directly by atomic absorption spectrometers using a nitrous oxide-acetylene flame. The analysis for chromium(VI) was performed by using the ADPC/MIBK procedure described in Section 5.6.

The suspended particulate samples were processed according to the acid extraction procedure described in Section 5.5. In a few instances, where the acid extraction scheme would not dissolve the sample, a standard sodium carbonate fusion technique was employed.

5.4 ANALYSIS PROCEDURE FOR ORGANO-CHROMIUM COMPOUNDS

5.4.1 Air and Water Samples

The XAD resins employed for air and water sampling for organic chromium compounds were purified in a soxhlet extraction apparatus prior to sampling. The order of solvents and the extraction times for each solvent are given in Table 13.

Table 13. PREEXTRACTION ROUTINE FOR XAD RESIN

Solvent	Time
Distilled water	24 hr
Methanol	24 hr
Ethyl ether	8 hr

After the extractions with ether, the XAD was transferred to a vacuum desiccator and dried under vacuum for 24 hours. The XAD resin was then placed into traps for field sampling.

Upon completion of sampling the XAD resin was removed from the traps and placed in a previously extracted paper thimble. The thimble and contents were then soxhlet extracted with 250 ml of ethyl ether for 4 hours. The volume of ether remaining after the extraction was determined and the XAD extract was placed in a tightly sealed glass bottle. Analysis for chromium in the ethyl ether extract was performed by flameless atomic absorption spectroscopy.

5.4.2 Sewage Treatment Plant Sludge

Two sludges from sewage treatment plants were processed according to the ether extraction scheme outlined in Figure 8. The inorganic fraction was extracted with hydrochloric acid and nitric

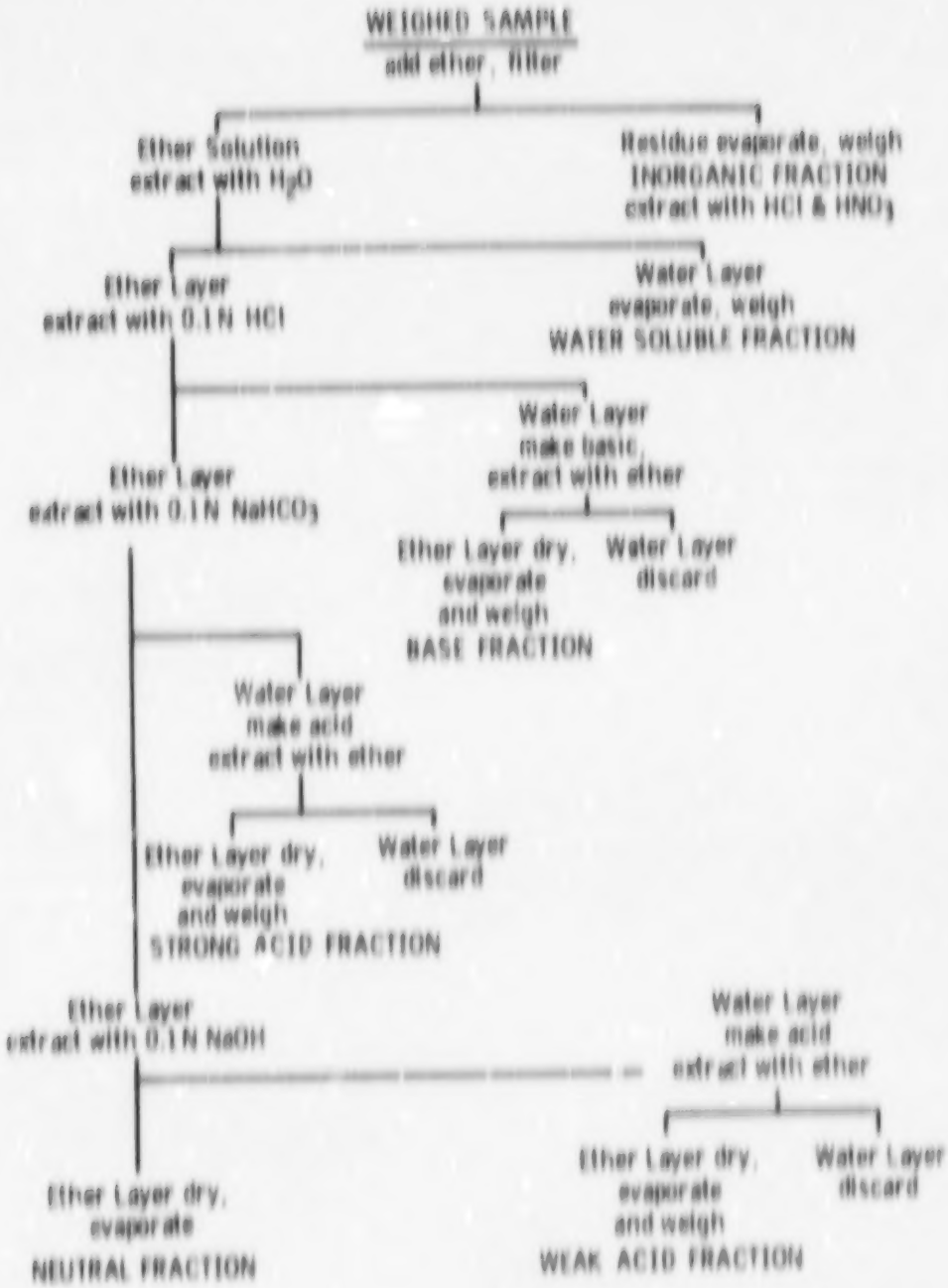

Figure 8. Liquid Extraction Scheme
For Organic Compounds.

acid as described in Section 5.5. Each organic fraction was digested with a 1:1 mixture of H_2SO_4 and HNO_3. Four milliliters of acid mixture was added to each fraction. The fraction was heated to fumes, quantitatively transferred to a 25.0-ml volumetric flask, diluted with distilled, deionized water, and analyzed by atomic absorption.

5.5 SAMPLE PREPARATION - ACID EXTRACTION PROCEDURE

The procedure herein described is a modification of that described by Thompson, Morgan and Ferdue (10). This procedure was used to extract chromium from soil, high-volume air filters and water-insoluble suspended particulate.

Procedure

Soil (15 g), a portion of a high-volume filter (17.8 cm x 5.0 cm), or a filter containing water-insoluble particulate was dried at 60°C to constant weight, placed in a Pyrex boat and low temperature ashed at 425 watts in an LFE Corp.[8] LTA-505 Low Temperature Asher until the plasma discharge reverted to a blue color, indicating completion of ashing. The time required varied not only from sample type to sample type but from sample to sample within each type. Typical ashing times for each sample type are given in Table 14.

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(10) Thompson, R. J., G. B. Morgan, and L. J. Ferdue, "Analysis of Selected Elements in Atmospheric Particulate Matter by Atomic Absorption," Atomic Absorption Newsletter 9, 53-57 (1970).

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[8] LFE Corporation, Process Control Division, 1601 Trapelo Road, Waltham, Massachusetts 02154.

Table 14. TYPICAL ASHING TIMES FOR ENVIRONMENTAL SAMPLES

Sample	Typical Ashing Time (hr)
Soil	24
High-volume filters	2
Water-suspended particulate	1

Depending upon their physical state, the ashed samples were extracted by different methods using the apparatus shown in Figure 9. Samples which were permeable to the refluxing acid vapors (high-volume filters) were quantitatively transferred to a 25-mm Pyrex extraction thimble (coarse grade). The extraction thimble was then placed into the extraction apparatus shown in Figure 9 which had been previously charged with 8 ml of 19% HCl and 32 ml of 40% H_2O_2. The flask was fitted with an Allihn condenser. The acid was refluxed over the sample for 3 hours. The Allihn condenser was removed and the acid extract was concentrated to 20 ml on a hotplate. The samples which exhibited a low permeability to the refluxing acid (soil, sediment) were placed directly into the flask. After extraction was complete these samples were quantitatively filtered prior to the concentration step. After cooling, the acid concentrates of all samples were quantitatively transferred to 100-ml volumetric flasks, diluted with distilled water, and transferred to 200-ml polyethylene sample bottles for storage until analyzed.

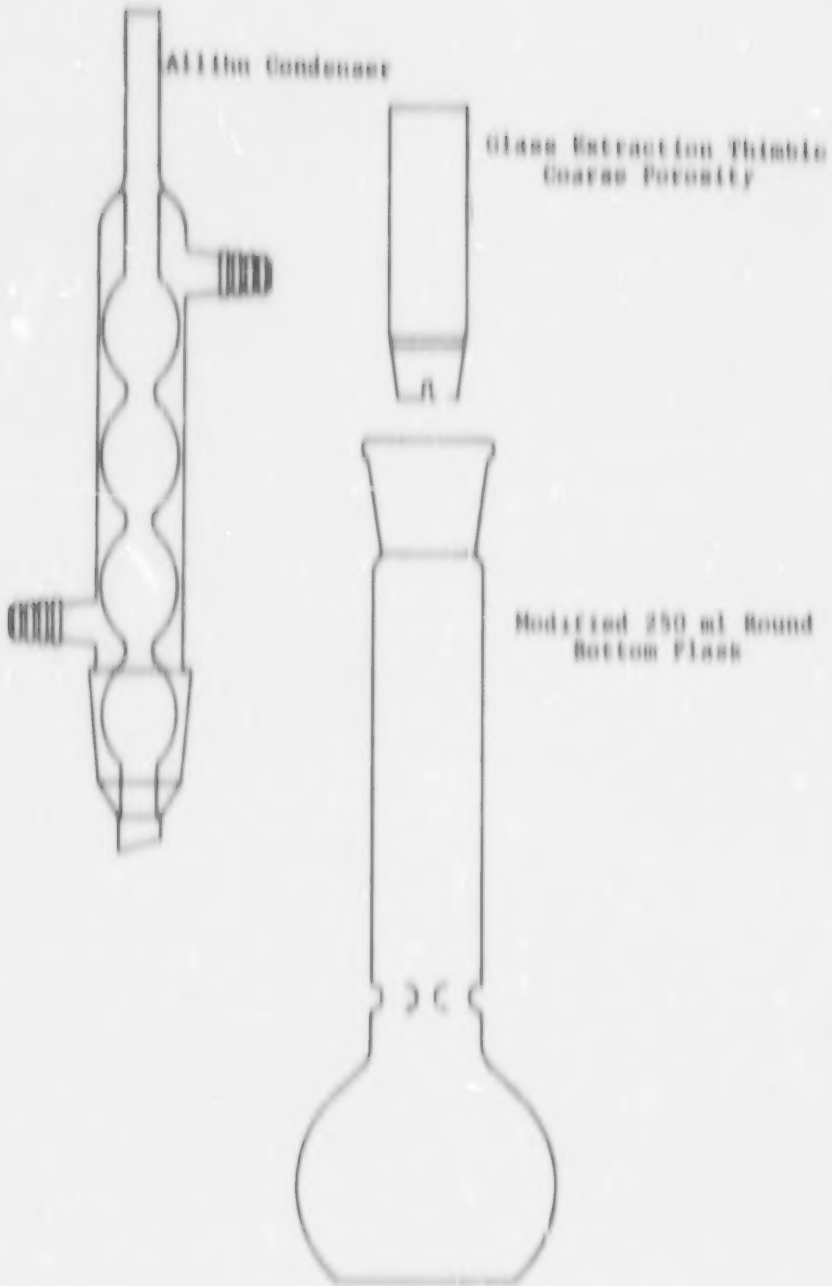

Figure 9. Acid Extraction Apparatus.

5.6 METHYL ISOBUTYL KETONE/AMMONIA PYRROLIDINE DIETHIOCARBAMATE EXTRACTION PROCEDURE FOR CHROMIUM(VI)

The procedure is a modification of that described by Midgett and Fishman (11) where the major change was that the extraction was carried out in ≈60 ml bottles or screw-top test tubes. The methyl isobutyl ketone (MIBK) was distilled in glass and obtained from Burdick and Jackson Laboratories, Inc.[8] A 5% solution of ammonium pyrrolidine dithiocarbamate (APDC) was prepared fresh daily by dissolving 5.0 g of APDC in 100 ml of distilled deionized water and extracting the solution with successive portions of MIBK until the organic layer was clean. Normal sodium hydroxide (NaOH) was prepared by dissolving 40 g of NaOH in distilled deionized water and diluting to exactly 1 liter. Tenth normal NaOH was prepared by pipeting 10.0 ml of 1.0N NaOH into a 100.0-ml volumetric flask and diluting to the mark with distilled deionized water. Tenth normal nitric acid (HNO_3) was prepared by pipeting 6.4 ml of concentrated nitric acid into a 2-liter volumetric flask and diluting to the mark with distilled deionized water. Methyl violet indicator (0.1%) was prepared by dissolving 0.1 g of the indicator in 50 ml of 95% ethanol and diluting to 100.0 ml with distilled deionized water.

The determination of chromium(VI) in sample extracts or water was accomplished by first pipetting exactly 20.0 ml of sample into an acid-cleaned 60 ml bottle. After adding 2 drops of 0.1%

(11) Midgett, M. R. and M. J. Fishman, "Determination of Total Chromium in Fresh Waters by Atomic Absorption," Atomic Absorption Newsletter 6, 128-131 (1967).

[8] Burdick and Jackson Laboratories, Inc., 1953 S. Harvey Street, Muskegon, Michigan 49442.

methyl violet indicator, either NaOH or HNO_3 was added until the indicator changed from yellow to blue-blue green (pH = 2.4-2.6). Then, 5.0 ml of 5% APDC solution, 3.0 ml of saturated Na_2SO_4 solution, and 20.0 ml of MIBK were pipetted into the 60 ml bottle. The bottle was tightly capped and shaken on a wrist-action shaker for 3-5 minutes. The chromium(VI) was then determined by aspiration of the top organic layer into the C_2H_2/air flame of the Varian AA-6 atomic absorption spectrophotometer. The concentration of chromium(VI) was obtained from a suitable calibration curve prepared by extracting standard solutions employing the same procedure.

In some cases where low levels of chromium in water were suspected, a 2-liter portion of the water sample was extracted by this procedure using a separatory funnel.

5.7 VARIAN AA-6 INSTRUMENT PARAMETERS FOR CHROMIUM

Chromium can be determined by atomic absorption spectroscopy employing either an air-acetylene or nitrous oxide-acetylene flame. In this study air-acetylene flames were used except when a nitrous oxide-acetylene flame was required to reduce interference by cobalt, nickel, iron, copper, barium, aluminum, magnesium, calcium, etc., which were present in some sample matrices. All of the total chromium data for soil, water and filter samples were obtained using the nitrous oxide-acetylene flame. An air-acetylene flame was employed for the determination of chromium(VI) via the MIBK/APDC extraction procedure. Figures 10 and 11 show the typical calibration curves obtained by each technique. Table 15 presents the instrument parameters employed on the Varian AA-6 spectrometer.

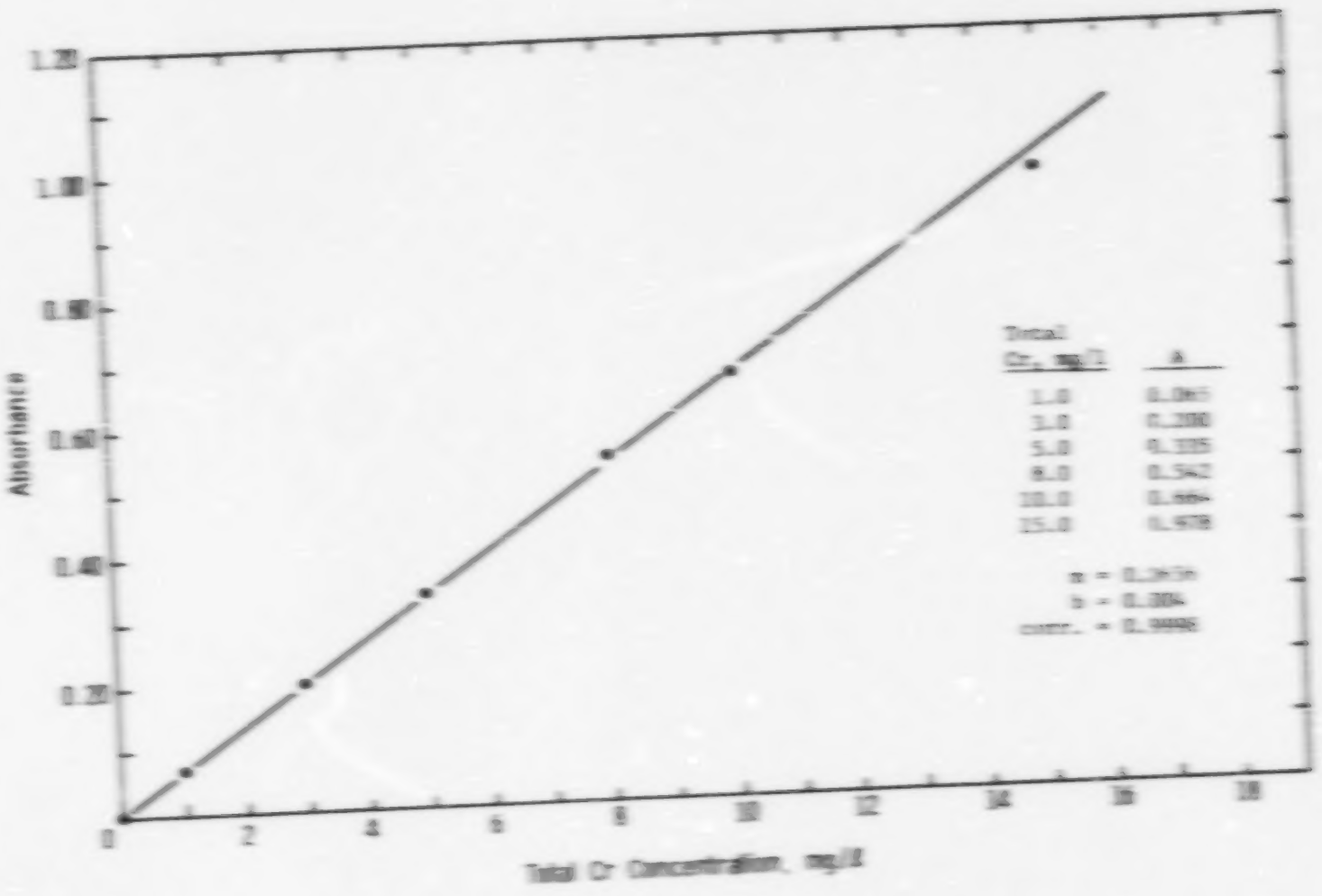

Figure 11. Calibration Curve for Total Chromium by Atomic Absorption (Air-C$_2$H$_2$ Flame).

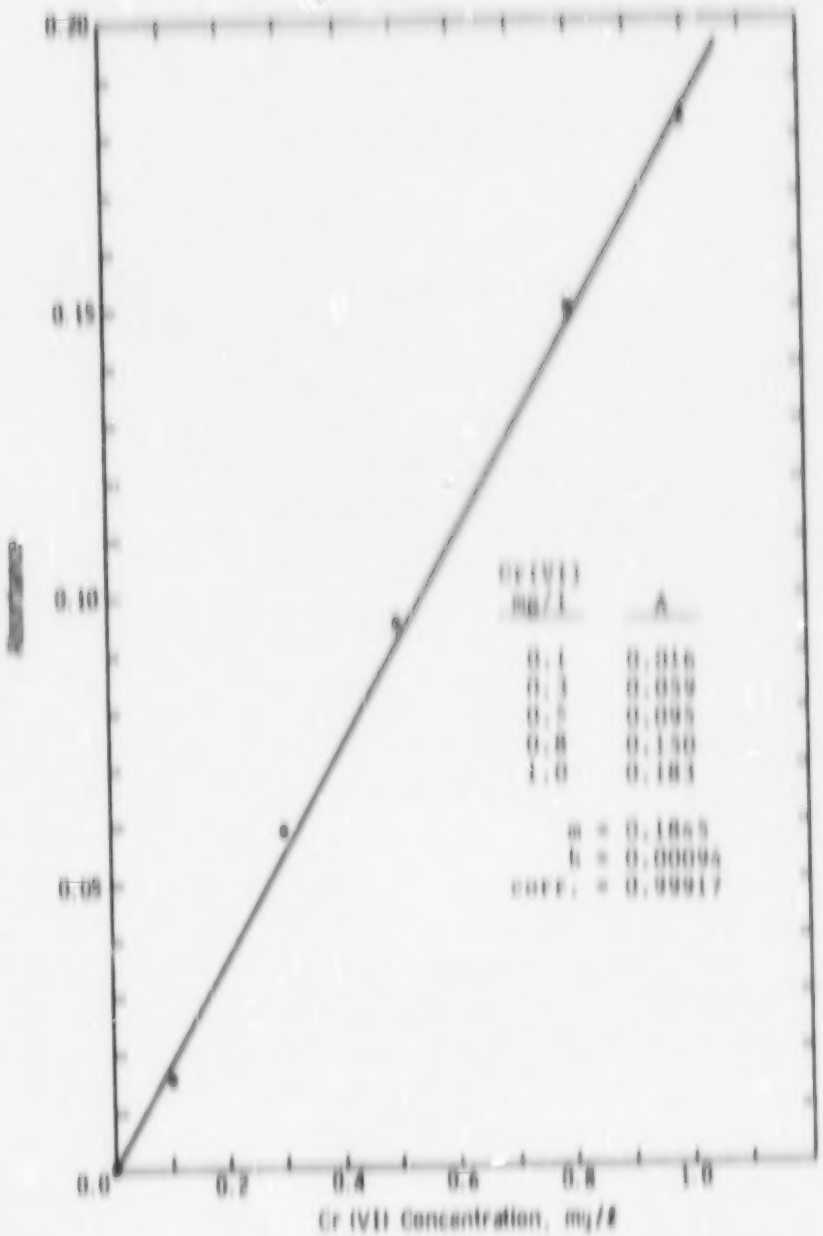

Figure 11. Calibration Curve for Cr(VI) by Atomic Absorption (N_2O/C_2H_2 Flame).

Table 15. INSTRUMENT PARAMETERS FOR VARIAN AA-6

Wavelength = 357.9 nm
Spectral band pass = 0.2 nm
Lamp current = 5 mA

Flame conditions:	N_2O/C_2H_2	Air/C_2H_2
Fuel setting (M-80 gas box)	6.5	1.5
Oxidant setting (M-80 gas box)	5.3	5.3
Detection limit	0.005 mg/l	0.005 mg/l

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2. Resnik, Richard B. "Source Assessment: Flat Glass Manufacturing Plants," EPA 600/2-76-032b March 1976, pgs. 122-126.

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4. Martin, D. O. and J. A. Tikvart, "A General Atmospheric Diffusion Model for Estimating the Effects of Air Quality of One or More Sources," presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minnesota, June 23-27, 1968, 18 pp.

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10. Thompson, R. J., G. B. Morgan, and L. J. Perdue, "Analysis of Selected Elements in Atmospheric Particulate Matter by Atomic Absorption," Atomic Absorption Newsletter 9, 53-57 (1970).

11. Midgett, M. R. and M. J. Fishman, "Determination of Total Chromium in Fresh Waters by Atomic Absorption," Atomic Absorption Newsletter 6, 128-131 (1967).

APPENDIX A

SAMPLING AND ANALYSIS OF CHROMIUM AND LEAD AT MINERAL PIGMENTS CORPORATION, BELTSVILLE, MARYLAND

Mineral Pigments Corporation
7011 Muirkirk Road
Beltsville, Maryland 20705

1. PRESAMPLING SURVEY

Mineral Pigments Corporation, 7011 Muirkirk Road, Beltsville, Maryland 20705, was chosen for a presampling survey as a typical chromium pigment producer in accord with two criteria discussed in the body of this report (2.2.1). A survey visit was conducted on 18 and 19 August 1976 by MRC personnel. Mr. Fred Wrocsonski, Vice President and Mr. Yassan Allah, Plant Superintendent, were contacted and through their cooperation a description of the processes inside the plant was obtained and the emissions control system was observed. The plant makes chromium oxide, lead chromate, molybdate orange and zinc chromate pigments. Some processes are continuous but others are run by the batch. Normally, the plant operates 24 hour/day, 6 days/week.

The plant site is about 3 km north of Beltsville, Maryland which is in turn just north of the I-495 beltway surrounding Washington, D.C. The area surrounding the plant is wooded and the terrain is that of rolling hills. The area is rural with little concentration of population in the immediate vicinity of the plant. Beltsville itself is not heavily industrialized.

The plant consists of a collection of buildings, many of which show stains of yellow or green pigments, especially on their roofs. The buildings occupy a lot estimated to be 100 m x 200 m which is bordered on the west by a railroad, on the north by a two-laned paved road (Old Baltimore Pike), on the east by a paved access street to an industrial park and on the south by an unpaved alley which provides a driveway for three occupied homes.

The industrial park to the south of the plant site is mainly warehouses and there is no industry which should constitute a

a major chromium or lead emission. The railroad and adjacent highways may cause some heavy metal (e.g. Pb) emissions. One of two warehouses had dumped large amounts of vermiculite (discarded packing material) in the area and this material may affect some of the soil and sediment characteristics. The terrain to the northeast of the plant is level and occupied by a junk car lot, a brick manufacturing facility and a claypit. No visible emission points were observed from the brick manufacturing operation.

During the visit, no visible air emissions were observed. This was also the case during the actual sampling period 28-29 October but a clearly visible yellow plume was observed from a rooftop steam vent for several days during an aborted sampling attempt on 21-22 October 1976. At this time, the air emission had prompted D. W. Palmer of the Maryland Department of Health and Mental Hygiene, Bureau of Air Quality, (301-383-3147), to temporarily halt that process within the plant while new scrubbers were installed.

The plant has three air emission points, all of which are controlled by scrubbers. Two of these are rooftop vents approximately 7.6 m from the ground and the third is a chromium oxide kiln stack about 23 m in height. At the time of the 21-22 October visit, the kiln was not in operation but it was in operation during the sampling period.

Also during the aborted sampling visit of 21-22 October, Mr. F. A. Bisegar of the Maryland Water Resources Administration, (301-267-5551), showed the sampling party the liquid outfall from the plant.

Wastewater treatment consists of double clarifying with alum and flocculants and a sump at the southwest corner of the lot. The

sump did not appear to be an integral part of the treatment system but rather appeared to be used to hold runoff from the yard and occasional grease discharges from the plant. The outfall which is usually turbid and yellow in color passes over a V-notch and falls into an underground storm drain at the southwest corner of the lot. It follows the storm drain for about 150 m, past one surface-access manhole, and empties just below the water level into an unnamed stream which is nominally 2 to 3 m wide and 5 to 10 cm deep. It is estimated that the outfall is about 10% of the creek flow at this point. The creek runs to the south parallel to the railroad in a broad, rocky streambed with very little organic material or aquatic life. Approximately 1 km from the plant the stream flows into a broad, shallow pond/marsh where cattails, grass, and algae scum are observed. Above the plant outfall there is considerable organic material in the water and on the bottom, but the stream below the outfall is not inhabited by water plants and algae until the pond/marsh is reached. Occasionally, yellow colored patches of sediment are observed at points along the streambed over a kilometer below the outfall.

Soon after the preampling survey articles published in the Washington Post (1) indicated that the Mineral Pigments plant was under close surveillance by the Occupational Safety and Health Administration for alleged violations of federal health and safety standards for lead exposure. Dr. Vincent DeCarlo, the Contract Project Officer, requested that the Beltsville, Md. site be sampled. After one sampling trip (21-22 October) during which the plant was shut down, sampling was accomplished on 28 and 29 October 1976.

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(1) Washington Post, Monday, September 13, 1976 pp A1-A2.

2. SAMPLING AND ANALYSIS

2.1 AIR SAMPLES

The air sampling tactics employed at this site involved setting up a downwind array of high-volume samplers to sample the plume during a period of steady wind conditions and the use of a group of perimeter high-volume sampler to collect emissions over a longer (24 hour) period during which wind conditions have a larger variability. The array arrangements are shown in Figures 1 and 2. The downwind array (samplers 5-8, with sampler 1 serving as a background sampler) was set up after observing the existing wind patterns and assessing the atmospheric stability class as discussed in Section 3.1 of the main report. These data were used in the Martin-Tikvart (2) air diffusion model to calculate the emission rate of the plant. From the observed plume sampling results, the emission rates for Cr and Pb were 18 mg/s and 49 mg/s, respectively. These values apply primarily to the rooftop vents and do not include the Cr(III) emissions from the kiln stack. During the plume sampling, the wind held strongly at 305 degrees for 260 minutes with maximum deflections of +22° and -25°. The wind velocity (10 m high) was 7.6 km/hr ranging from less than 5 to a maximum of 24 km/hr.

The plume sampling was discontinued after 260 minutes when the wind direction drifted off the downwind sampler array. At that point, the filters on samplers 1 and 8 were replaced and sam-

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(2) Martin, D. O., and J. A. Tikvart "A General Atmospheric Diffusion Model for Estimating the Effects on Air Quality of One or More Species," presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minnesota June 25-27, 1968 18 pp.

Figure 1. Shovel Figures for Sampling Sites.

ters 1, 2, 4 and 8 represented the perimeter samplers for a total sampling period of 24 hours. Results from the two filters employed on samplers 1 and 8 were summed in order to obtain the perimeter chromium and lead loading over the full 24-hour period. (Note that sampler 8 was substituted for 3 in the ideal perimeter array presented in Figure 2).

Each of the downwind plume array samplers collected 295 m^3 of air over the downwind sampling period while samplers 1, 2, 4 and 8 collected 1609 m^3, 1736 m^3, 1724 m^3 and 1592 m^3 of air, respectively, over the perimeter sampling period. The average barometric pressure during the sampling period was 1.01 atmospheres and the wet and dry bulb temperatures were 51°F and 49°F, respectively.

Table 1 presented the lead and total chromium results in mg/m^3 at each of the sampling locations. As one would expect, the downwind array collected a much greater concentration of airborn lead and chromium than did the perimeter samplers with the maximum concentration found on the centerline samplers (samplers #5 and #7). The upwind sampler (#1) did not collect a measurable quantity of either lead or chromium. Since the total particulate emissions include lead chromate, zinc chromate and chromic oxide, no attempt has been made to further interpret the lead/chromium ratios in the analysis of the airborne particulate. It should be noted that the array was positioned so that emissions from the roof vents would be collected rather than from the chromium oxide kiln stack. The rationale employed in this decision was that the emissions from the kiln stack would be primarily trivalent chromium and not hexavalent chromium or lead which are of greater concern from a health hazards viewpoint.

The diffusion model predicts maximum ground level particulate concentrations from the kiln stack at about 1.6 km from the

Table 1

Air Sampling Results

Sample	Total Pb $\mu g/m^3$	Total Cr ([Cr(III)+Cr(VI)]) $\mu g/m^3$	Cr(VI)* $\mu g/m^3$
Downwind Plume (Sampling Array) (250' site)			
Site #1 (Background)	<1.345>	<0.345>	<0.0009>
Site #5	34.1	8.93	0.713
Site #6	0.622	3.33	0.340
Site #7	28.3	13.5	2.09
Site #8	20.85	1.58	0.396
Perimeter Array (24 hr)			
Site #2	0.815	0.026	0.003
Site #3	4.48	1.78	0.0865
Site #4	0.451	0.136	0.00432
Site #9	4.32	0.618	0.038

+ Limits of detection

* As noted in the experimental section, the extraction procedure inadvertently converts variable amounts of Cr(VI) to Cr(III). Thus, while total chromium results appear to be very reliable, the Cr(VI) values are at best lower limits and are probably only indications of the presence of Cr(VI). Note that it is also not justified to assume that total Cr equals Cr(VI) though obviously the total chromium values are upper limits on Cr(VI).

plant site. The roofline sources, on the other hand, would yield maximum ground level concentrations less than 10 m from the point of emission. One evidence for this effect can be noted in the analysis results on the #5 and #7 filters where the lead concentration is decreasing with distance from the plant while the chromium concentration is increasing. From the diffusion model one would expect a drop off in concentration by a factor of 19% from 120 m to 150 m for particulate emitted from the roof vents. This compares with an experimental drop off of 17% between 125 m and 150 m.

As discussed in the body of this report, the values for concentration of Cr(VI) are not meaningful since Cr(VI) was converted to Cr(III) in the acid digestion step of the analysis. The values for Cr(VI) are included here only as an indication that some hexavalent chromium was present in the initial samples.

2.2 WATER SAMPLES

The water samplers were set up as shown in Figures 3 and 4. A sample of the effluent was obtained before it entered the ground (Site No. 1). Sites 2, 3 and 4 were taken in the stream before it enters the pond. Site No. 5 was taken after the pond.

The water sampling results are listed in Table 2. Since acid digestion was not required in this case, the Cr(VI) results are valid. These results represent the soluble species while the suspended species results are shown in Table 3. Examination of the Pb/Cr atom ratio in the suspended particulate indicate that this material is not $PbCrO_4$ (Pb/Cr=1.0).

2.3 SEDIMENT SAMPLES

Samples of stream sediment were taken at the same location as the water samples with the exception of the plant effluent sample

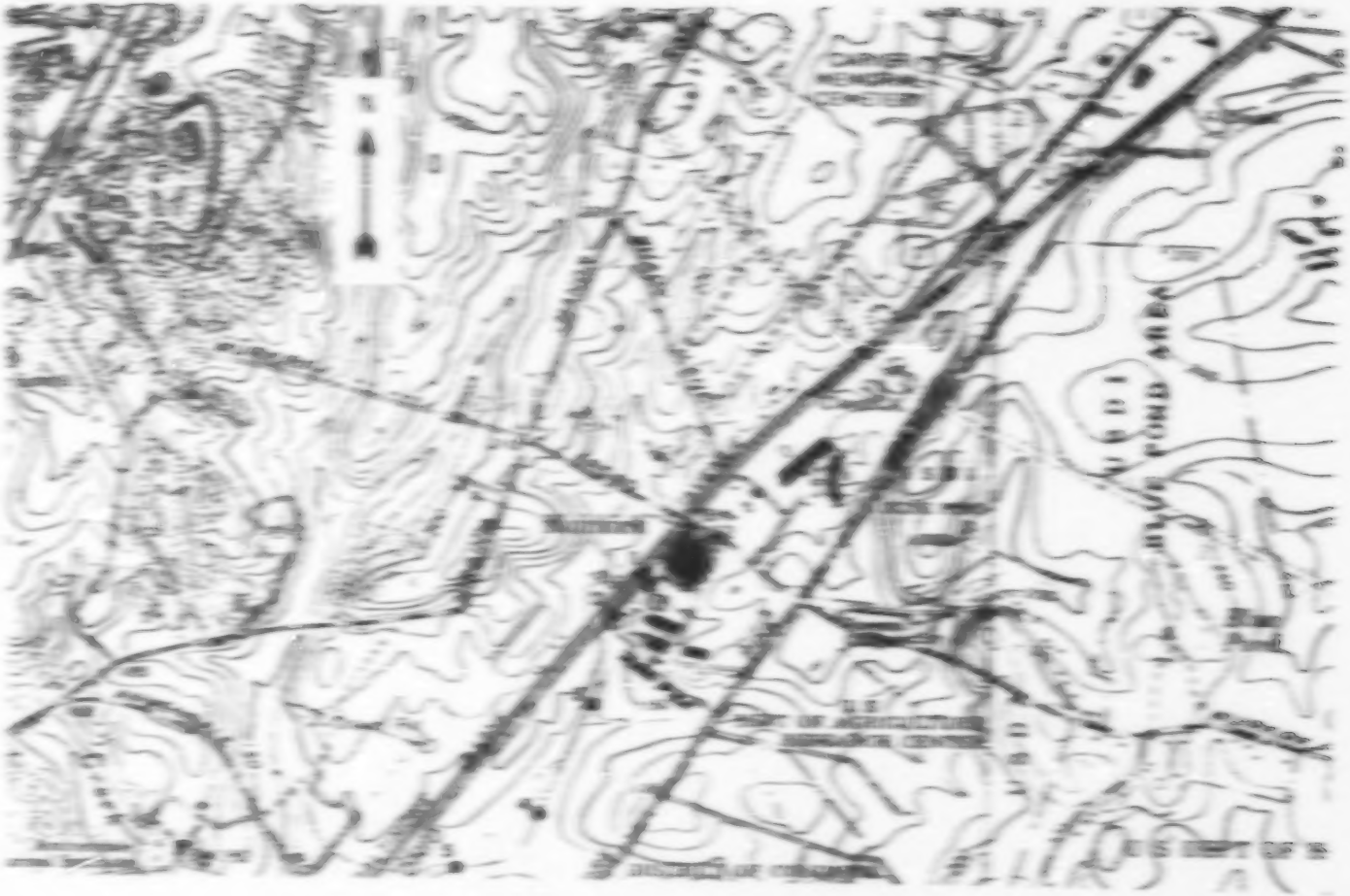

Figure 1. [illegible] Experiment Station.
Scale: 1 cm = 125 m

Sample	Total P (mg/L)	Total N (mg/L)	pH (S.U.)
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

Table 2

Water Sampling Results

Sample	Total Pb mg/l	Total Cr mg/l	Cr(VI) mg/l	Cr(VI)/ Cr (Total)
Site #1	<0.05	3.23	2.10	0.6[illegible]
Site #2	<0.05	3.32	1.35	0.4[illegible]
Site #3	<0.05	2.51	0.85	0.3[illegible]
Site #4	<0.05	1.76	0.24	0.1[illegible]
Site #5	<0.05	0.92	0.82	0.8[illegible]

Table 3

Particulate in Water

Sample	Total Pb mg/l	Total Cr mg/l	Atom Ratio Pb/Cr
Site #1	34.1	59.6	1:7.0
Site #2	18.8	3.98	1:0.9
Site #3	2.5	6.98	1:11
Site #4	1.51	1.33	1:3.7
Site #5	0.089	0.084	1:1.8

site (#1). These locations are shown on the topographic map in Figure 5, and on a sketch in Figure 6.

The results of the sediment sampling are listed in Table 4. These results also indicate that chromium in the sediment is not in the form of $PbCrO_4$.

Table 4

Sediment Sampling Results

Sample	Total Pb ug/g	Total Cr ug/g	atom ratio Pb/Cr
Site #1	26.9	43.8	116.6
Site #2	750.2	668.3	113.0
Site #3	111.7	68.9	112.3
Site #5	68.1	65.66	113.8

3.4 SOIL SAMPLES

The optimum sampling sites for soil samples at Mineral Pigments Corporation were predicted by the diffusion model. Ground level concentration isopleths around the plant site were predicted from seasonal and annual meteorological data for both the roofline emission points and the stin stack effluent. Areas of maximum ground level concentration were predicted at 1° and 157° from due north. Figure 7 presents the soil sample sites on the topographical map and Figure 8 shows them on the plant diagram. Sites #1 and #2 were located 120 m and 370 m respectively from the plant on the 157° line. Sites #3 and #5 were located 490 m and 120 m respectively from the plant on the 1° line. Site #5 was located 210 m from the plant on a 280° line and was taken to serve as background. The soil sampling results are shown in Table 5. All soil samples were taken to the same depth (7.6 cm).

A-19

Figure 5. Mineral Pigments Sediment Sampling Results.

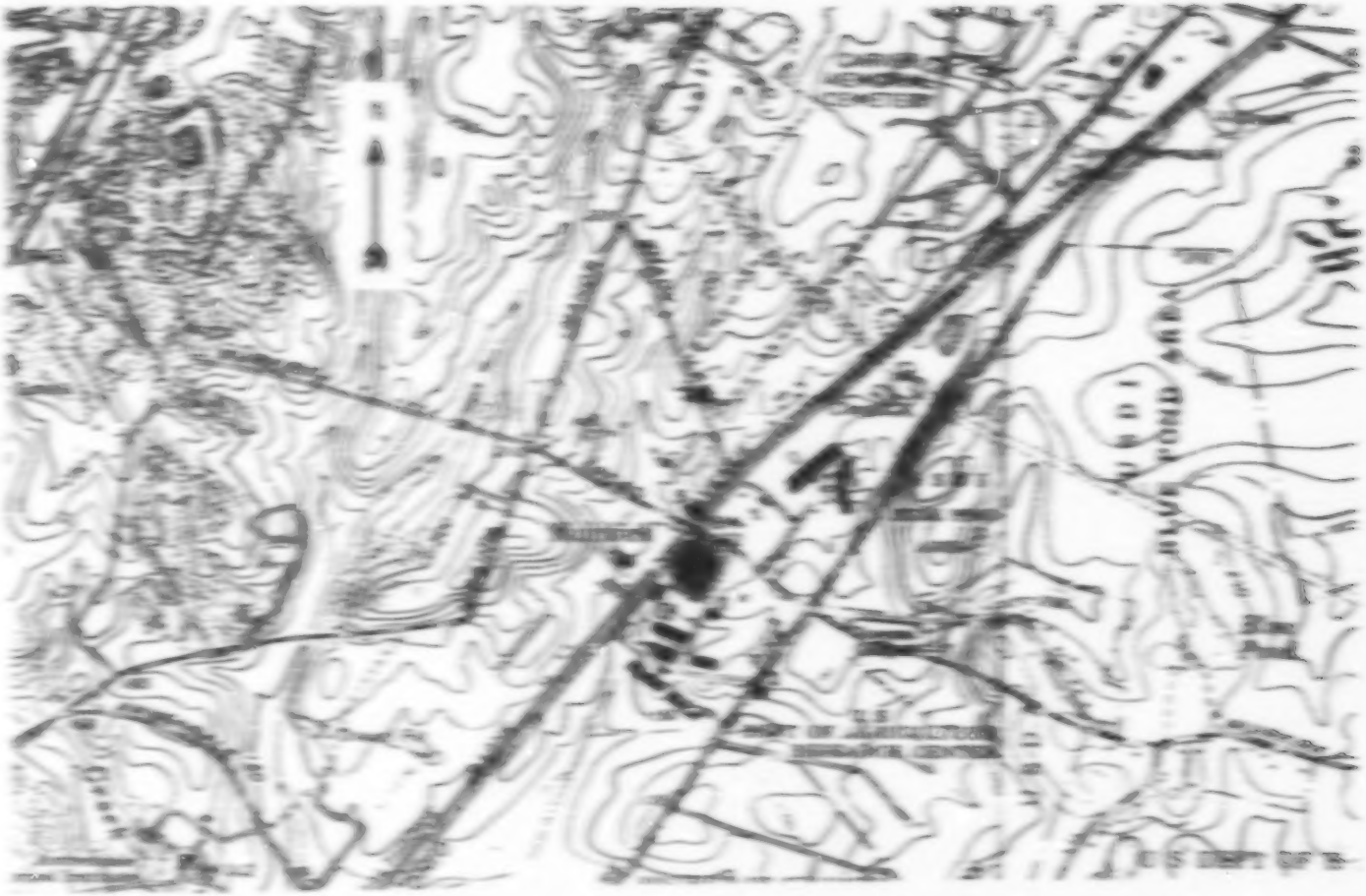

Figure 7. Mineral Pigments Drill Samples.
Scale: 1 cm = 195 m

Sample	Total Pb (ppm)	Total Cr (ppm)
Core #1	26,125	22,777
Core #2	51,687	30,622
Core #3	222,3	74,85
Core #4	32,9	27,5
Core #5	301,6	41,32

Figure 2. Ethanol Pigments Soil Sampling Results.

The soil type was similar in all areas sampled with a ground cover of grass.

Table 5

Soil Sampling Results

Sample	Total Pb (ug/g)	Total Fe (ug/g)
Site #1	76.15	22.77
Site #2	51.97	30.62
Site #3	220.3	28.95
Site #4	52.9	27.8
Site #5	301.6	51.32

When one compares these data with trends predicted by the diffusion model, a discrepancy is apparent. The model would predict higher soil concentrations of lead at Site #1 compared to Site #2. This discrepancy is most probably due to historical automobile traffic on Old Baltimore Pike where the #2 soil sample was taken.

APPENDIX B

SAMPLING AND ANALYSIS OF CHROMIUM AT
HERCULES, INCORPORATED,
GLENS FALLS, NEW YORK

Hercules, Incorporated
Lower Warren Street
Glens Falls, New York 12801

1. PRESAMPLING SURVEY

1.1 Description of the Plant Site

Hercules, Inc., located on Lower Warren Street in Glens Falls, N.Y. was chosen for a presampling survey as a typical chromium pigment producer in accord with the criteria discussed in the body of this report (3.2.1). A survey visit was conducted on 15 September 1976 by personnel of Monsanto Research Corporation (MRC). Contacts were made with Mr. Gary Dunn, Assistant Plant Manager. The plant management chose not to cooperate with the MRC personnel during the survey visit. As a consequence, little information was obtained about plant processes and operations.

The original facility was constructed in 1900, and the production of chromium pigments was started in 1920. The plant produces chromium oxide, lead chromate, molybdate orange, zinc chromate and compounded chrome pigments. Normally, the plant is in continuous operation (24 hours/day, 7 days/week).

Numerous buildings, some of which are interconnected, comprise the plant facility. The buildings are located on a lot estimated to be 150 m x 900 m. Approximately 2/3 of the northern boundary is adjacent to the Glens Falls Feeder Canal, whereas 1/3 of the boundary is next to Route 254. Route 32 is immediately north and adjacent to the Glens Falls Feeder Canal and intersects Route 254 on the northern side of the canal and immediately north of the major concentration of plant buildings. The east section of the lot is a large automobile parking area and is bounded partially by a gully (approximately 5 meter depression) which can serve as a storm drain and by a driveway

serving a single family dwelling. The southern border is the Hudson River. On the west is a paved, two-lane road which provides access to a portland cement plant and a quarry. Figure 1 shows the plant location (shaded) on a topographic map.

The plant is located on the flood plain of the Hudson River. A railroad spur track is located on the south side of the plant within the Hercules, Inc. property between the river and the major grouping of buildings. The general area to the north of the plant contains open fields bounded by trees, and small businesses and some single family dwellings adjacent to Route 32. To the east are located rows of houses paralleling Route 254. Gravel pits and quarries are located to the east, west and southwest. Located on the same floodplain and upstream of the Hercules, Inc. plant to the west are a portland cement plant and a sewage disposal facility.

Emissions from the cement plant and quarries can potentially affect the soil and sediment characteristics of the area. The effect of the sewage disposal facility on the water and sediment are unknown and would depend on the types of waste processed at the facility, the methods of disposal, and the efficiency of its operation.

During the visit, intermittent (approximately every 20 min) orange and yellow plumes (duration of approximately 4 min) were observed as emissions from 2 stacks. Building roofs and certain stacks were yellow and orange in color. Several steam plumes and a plume from a large boiler plant stack were also visible. One local resident located just north of the plant complained that the black shingles on his roof are turning green and that snow during the winter turns blue around the plant.

Figure 1. Hercules Inc. Plant Site (shaded area).
Scale: 1 cm = 215 m

Actual emission points are not known because of lack of cooperation from the plant management. There are roof-type stacks with a total height of approximately 15 m from the ground. The boiler stack is approximately 45 m in height. No control devices were visible; lack of cooperation from plant personnel precludes knowledge of whether or not any exist.

The wastewater treatment facility was installed two years ago. Process wastes are neutralized (pH ~7) by lime treatment; Cr(VI) is reduced by using SO_2. Water effluent from the treatment process is discharged continuously into the Hudson River at a rate of approximately 13000 m^3/day. Sludge generated in the treatment plant is retained on-site in a land-fill.

Outfall is discharged from a concrete pipe having an internal diameter of approximately 1 m. The water cascades down the river bank (approximately 8 m drop) into the Hudson River. The outfall flow is extremely rapid. At the point of plant discharge, the river is divided by an island; the river branch (approximately 15 m in width) passing the outfall moves slowly. Other than a small amount of pink foam, no irregular characteristics, e.g., color and turbidity, were noted at the outfall.

1.2 Description of Surrounding Area

The Hercules, Inc. plant is located in Glens Falls, N.Y. on the Hudson River approximately 70 kilometers north of Albany, N.Y. and 3-5 kilometers east of Interstate 87. The general area is rural and forested and the topography is hilly. Population is located principally along the Hudson River in two cities, Glens Falls (pop. 17,223) and Hudson Falls (pop. 7,997). A General Electric plant is located in Hudson Falls and pulp and paper industry exists throughout the area.

2. SAMPLING AND ANALYSIS RESULTS

Sampling of the Hercules, Inc. site was conducted on October 5-6, 1976. The types, conditions, locations and results for the samples collected during this time are contained in the following subsections.

2.1 Air Samples

The location of the plant site and the surrounding topography greatly limited the area in which the air sampling array (Section 3.1 of main report) could be assembled. This meant that only under very specific wind conditions could such an array be used. Unfortunately, lack of wind or improper direction precluded the use of the sampling array during the dates sampled. Due to the unfavorable conditions an alternative array of samplers that roughly surrounded the plant site was decided upon.

The locations of the high volume samplers are indicated on a topographical map (Figure 2) and a site sketch (Figure 3). Sampler 1 was located to the south of the plant site near a quarry on the opposite side of the Hudson River. Sampler 2 was located on the west perimeter of the site between the plant boundary and the portland cement access road. Samplers 3 and 6 were located to the north just across highway 32 from the plant and west of the intersection of highways 32 and 254. Sampler 8 was located to the north across highway 254 east of the intersection. Sampler 4 was located on the east perimeter across the small gully (see site description Section 1.1) on the north bank of the Hudson River. Samplers 5 and 7 were not used during the sampling period. Sampling times

Figure 2. Hercules Air Sample.
Scale: 1 cm = 225 m

ranged from 25.50 hours (1733 m^3) to 28.25 hours (1919 m^3).

Wind data were obtained during the sampling period, and a wind rose calculated from these data is included in Figure 3.

The results from the analyses of the air samples are contained in Table 1 and Figure 3. The highest total Cr concentration was obtained at Sites #8 and #1 which are north of the main building concentration. However, Site #6, also north, showed relatively low total Cr concentration. There seems to be no general correlation between the wind rose and the values obtained. The values for Cr(VI) should be taken only as an indication of its presence and not as true concentrations due to conversion of Cr(VI) to Cr(III) in the preanalysis acid extraction procedure (see Section 5.1 of main report).

Table 1

Air Sampling Results

Sample	Total Cr ($\mu g/m^3$)	Cr(VI) ($\mu g/m^3$)
Site #1	0.14	0.10
Site #2	0.12	0.085
Site #3	0.37	0.008
Site #4	0.045	<0.002
Site #5	0.072	<0.032
Site #8	0.56	0.018

Figure 1. Vermiculite Air Sampling Results.

2.3 Water Samples

Water sampling sites were selected along the north side of the Hudson River as indicated on the topographical map (Figure 4) and the site sketch (Figure 5). Site #1 was located at the plant outfall. Site #2 was located approximately three stream widths (~40 m) downstream of the outfall at a point near the intersection of the streams flowing around the small island that is opposite the outfall. Site #3 was located approximately six stream widths (~90 m) downstream at the east perimeter of the plant site. Site #4 was located approximately 250 m upstream at the west perimeter of the plant site (at this point the Hudson River flows in a single channel).

Samples of approximately four liters were collected at each site using 2 types of commercial water samplers (Manning and Isco). Also employed was a water sampler designed by NRC which is discussed in Section 4.2 of the main body of the report.

Suspended particulate samples were obtained by filtering the water samples through an 0.45 um Millipore® filter as described in Section 4.2 of the main report. Analyses were performed as described in Section 5.1 of the main report.

The results for the water analyses (dissolved Cr) are shown in Table 2 and Figure 5. In all instances both the total chromium and Cr(VI) concentrations were below the detection limits of 0.05 mg/l and 0.0025 mg/l respectively. The total Cr results for suspended particulates are given in Table 3. The results are erratic showing measurable values at the outfall (Site #1, 23.6 ug/l) and Site #3 (38.0 ug/l) but values below detection limits at Sites #4 and #2. It is conceivable that irregular flow patterns created by the several small islands in the river could create the seemingly uncorrelatable results.

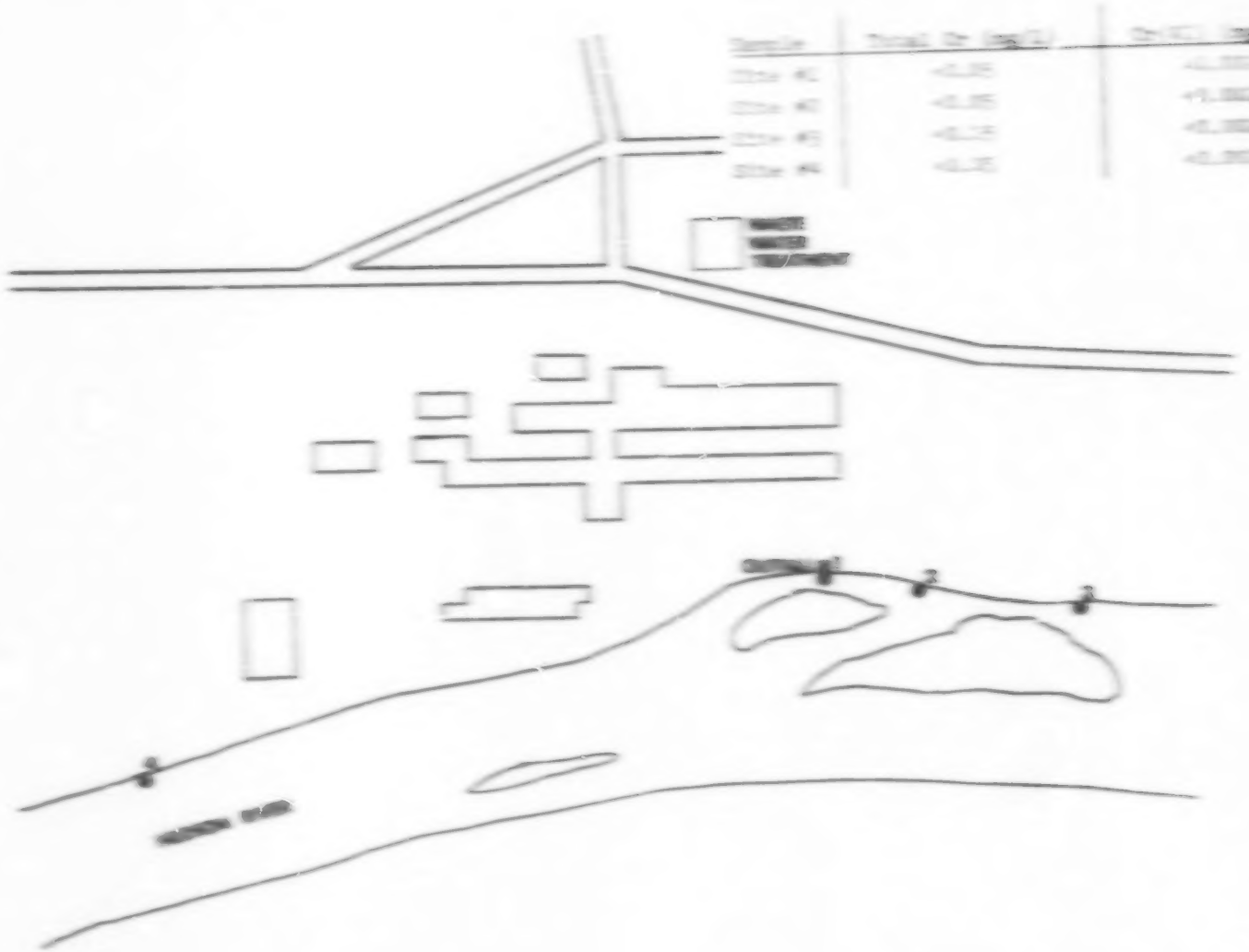

Figure 5. Vermilion Water Sampling Results.

Table 2

Water Sampling Results

Sample	Total Cr (mg/l)	Cr(VI) (mg/l)
Site #1	<0.05	<0.0025
Site #2	<0.05	<0.0025
Site #3	<0.05	<0.0025
Site #4	<0.05	<0.0025

Table 3

Particulates in Water

Sample	Total Cr (ug/l)
Site #1	23.6
Site #2	<10.0
Site #3	28.0
Site #5	<10.0

2.3 Sediment Samples

Sediment samples (approximately 100 ml each) were collected at the same locations as the water samples (Figures 4 and 5) according to the procedure described in Section 4.3 of the main report. Analyses were performed according to the procedure described in Section 5.2 of the main report.

The results from the analyses of these samples are given in Table 4. The upstream sampling site (Site #4) showed the lowest total Cr value (0.019 mg/g) while sites #1, #2, and #3 showed the opposite trend to that observed for the suspended particulate results. A possible explanation that is consistent with both the suspended particulate and sediment results is that Site #2 is located at a point of relatively low turbulence resulting in the settling out of particulate matter with attendant low suspended particulate Cr values and high (relative to Sites #1 and

Table 4

Sediment Sampling Results

Sample	Total Cr (mg/g)
Site #1	0.823
Site #2	3.59
Site #3	1.714
Site #4	0.019

#3) sediment values, while Sites #1 and #3 are located at points of higher turbulence resulting in larger amounts of suspended particulates and relatively lower concentrations of Cr in the sediment. Certainly this is the case at the outfall (Site #1) due to the turbulence it creates. The other variations of turbulence could be created by the flow around the several small islands as cited earlier.

2.4 Soil Samples

The optimum soil sampling sites for the Hercules, Inc. plant were predicted on the basis of the diffusion model (see Section 3.3 of main report) which indicated a maximum concentration area at 23° (relative to due north) and a secondary concentration at 160°. The locations of the soil sampling sites are indicated on the topographical map (Figure 6) and the site sketch (Figure). These sites were positioned relative to the main boiler stack since it was a convenient visual point of reference. Site #1 was located at 180° at a distance of ~600 m in a forest near the quarry on the opposite side of the Hudson River. Site #2 was located at 255° at a distance of ~550 m in a field between Hercules and the portland cement plant. Sites #3 and #4 were located at 23° to sample the predicted maximum concentration area at various distances. Site #3 was at a distance of ~100 m next to Route 254 opposite the plant, while Site #4 was at a distance of ~400 m in the yard of an old house. Site #5 was located at 160° at a distance of ~45 m between the railroad track and the river. This site was chosen to sample the predicted secondary concentration. The samples were collected and analyzed as described in Sections 4.3 and 5.3, respectively, of the main report.

The results from the analyses of the soil samples are given in Table 5 and Figure 7. As expected, Site #2, which lies the furthest from any predicted concentration maximum, had the lowest

Figure 6. Hercules Soil Samples.
Scale: 1 cm = 225 m

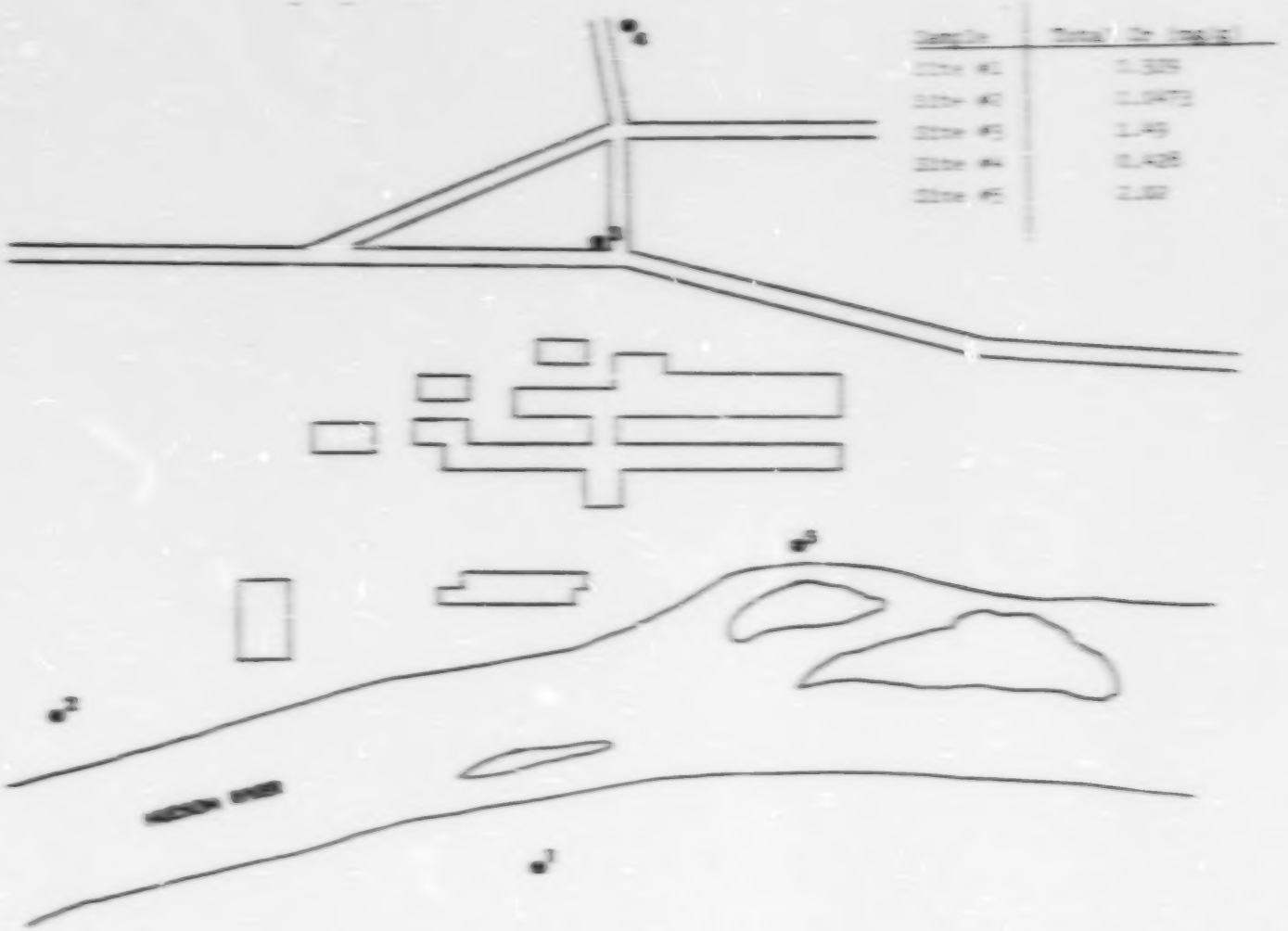

Figure 7. Hercules Soil Sampling Results.

total Cr concentration in the soil. The other four sites seem to follow a trend based on relative distance from the plant. Site #5, which was located along the predicted line of secondary concentration, had a higher total Cr concentration than Site #3 which was located along the predicted line of primary concentration. The explanation for this result probably lies in the fact that Site #5 is closer than Site #3 to the plant (45 m compared to 100 m). The fall off in concentration with distance can be seen by comparing the results from Sites #3 and #4.

Table 5

Soil Sampling Results

Sample	Total Cr (mg/g)
Site #1	0.329
Site #2	0.0473
Site #3	1.49
Site #4	0.428
Site #5	3.02

APPENDIX C

SAMPLING AND ANALYSIS OF CHROMIUM AT STOLLE CORPORATION DAYTON, OHIO

Stolle Corporation
1525 West River Road
Dayton, Ohio 45418

1. PRESAMPLING SURVEY

1.1 Description of the Plant Site

The Stolle Corporation, 1535 West River Road, Dayton, Ohio was chosen for a presampling survey as a typical chromium plating facility in accord with the criteria presented in the body of this report (2.2.2). Contacts were made with Mr. Al Lemon, Plant Superintendant. The plant management decided not to cooperate with MRC personnel during the study. Although no information was directly available concerning the plant processes, certain pertinent information was obtained from the NPDES permit.

According to the NPDES permit information (supplied in 1974), Stolle Corporation has 70 employees and operates on a 16 hour/day, 5 day/week schedule. Their business consists of all types of metal polishing, plating processes involving copper, nickel and chrome and anodizing aluminum. An indication of the volume of chrome plating done at the facility is given by the reported amounts of chromic acid (4,160 kg) and potassium chromate (90 kg) used during the period from January to June 1974. Their customers include automobile and household appliance manufacturers and various tool and die shops in the area.

The plant site is approximately 150 m x 150 m and consists of one large building and three holding ponds. It is bounded on the north by a construction equipment storage yard and a single residence dwelling, on the east and south by West River Road and the Great Miami River, on the southwest by a large open field and on the west by a railroad track, Danner Road and Madden Golf Course. Downstream at a distance of ~1000 m is the City

of Dayton, Guthrie Road Wastewater Treatment Plant. The Dayton Power and Light Company's Tate Station electrical generating facility is located ~1 km upstream of the Stolle plant site.

The Tate Station Power Plant is a coal burning facility and thus has potential for producing chromium emissions (Section 2.1.1 of main report). It is not known what contribution these might have on the samples taken in this study. The greatest likelihood for contamination from this source is in the soil samples which would reflect long-term contributions. However, since the Stolle Corporation site is to the southwest of the power plant and the prevailing winds are from the west and southwest, the likelihood of significant Cr contamination from the power plant is minimal. There is no other industry in the immediate area that would present possible Cr contamination.

There are several visible rooftop vents (air emission points) on the building, and white plumes (probably from heating) were observed during the time that air samples were being collected on February 10-11, 1977. No information was available concerning the presence or types of control devices on air emission points.

All chrome rinses are reportedly treated with the "chromaiator process." The steps of the treatment include addition of sodium hyposulfite, pH adjustment (to 6-9), and discharge into a settling pond. The contents of the settling pond are released over a period of ~8 hours. The treated wastewater is piped ~1200 m and discharged into the effluent stream from the Guthrie Road Wastewater Treatment Plant at a point ~50 m from where the treatment plant effluent enters the Great Miami River. The wastewater had a green color at the point of discharge. The discharge pipe and the wall of the treatment plant effluent channel near the discharge pipe are a distinctive dark green color. The total wastewater discharge from the Stolle plant is ~1200 m^3/day

which is diluted by the 210,000-230,000 m^3/day outfall from the Guthrie Road treatment plant before finally being discharged into the Great Miami River.

1.2 Description of Surrounding Area

The Stolle Corporation plant is located in the southwestern metropolitan Dayton, Ohio area approximately 15 km south of the intersection of Interstates 70 and 75. The immediate area around the Stolle Corporation site has a relatively low population concentration which increases as one moves toward the Dayton population center. Dayton is located in a river valley at the junction of the Miami, Mad, and Stillwater rivers. The general topography is flat. The metropolitan area has a population of ~865,000 and supports an impressive diversity of industry. There are some 850 plants located in Montgomery County producing over 1000 products with an estimated value of over $1 billion. Major industries in the area include automotive subassembly, appliance manufacturing and precision equipment.

2. SAMPLING AND ANALYSIS RESULTS

Sampling of the Stolle Corporation site was conducted on September 14-15, 1976 (water, sediment, and soil) and February 10-11, 1977 (air). The types, conditions, locations and results for the samples collected during these times are contained in the following subsections.

2.1 Air Samples

Figure 1 is an aerial view of the site with the positions of the air samplers indicated by the numbers in white. The air sampling array described in Section 3.1 and Figure 3 of the main report was used in sampling the Stolle Corporation site. The four-sampler downwind array (samplers 3, 4, 5 and 6) was positioned in the adjoining construction equipment lot with array dimensions indicated in Figure 2. The downwind array samplers were operated for periods ranging from 4.25 hours (288.7 m^3) to 5.83 hours (396 m^3). Wind data collected at 5 minute intervals during the sampling period showed an average wind velocity of 11.7 km/hr (ranging from 3 to 19 km/hr). Wind direction varied from -20° to +30° of the center line described by sampler 1, the source, and array samplers 3 and 5 (Figure 2). The barometric pressure was 750.6 mm Hg and wet and dry bulb temperatures were 41°F and 45°F respectively.

In addition to the downwind samples, perimeter samples were collected at sites 1, 2 and 3. The perimeter samples were collected for 19.33 hours (1305.4 m^3), 25.17 hours

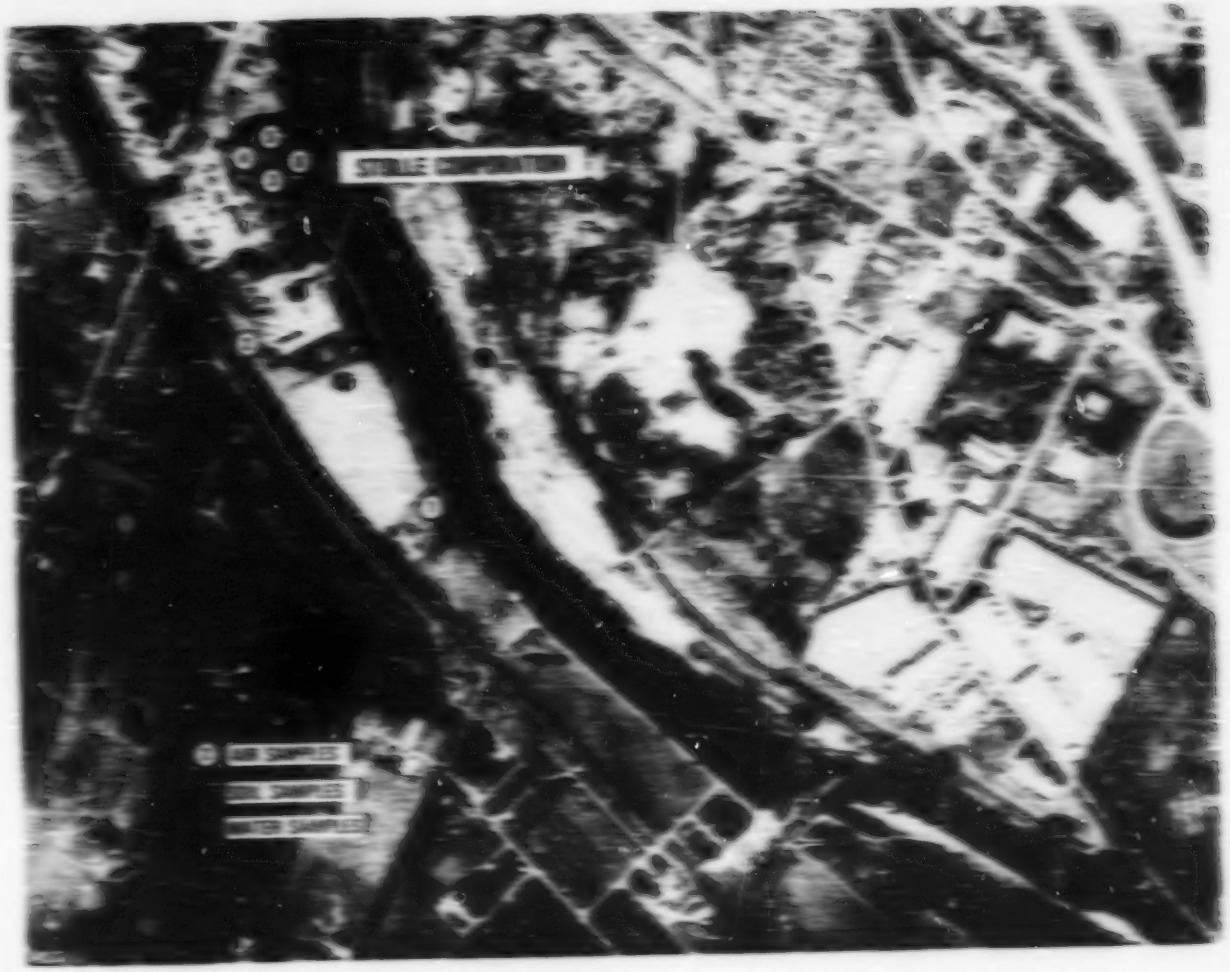

Figure 1. Aerial View of Shelle Corporation Site With Sampling Locations.

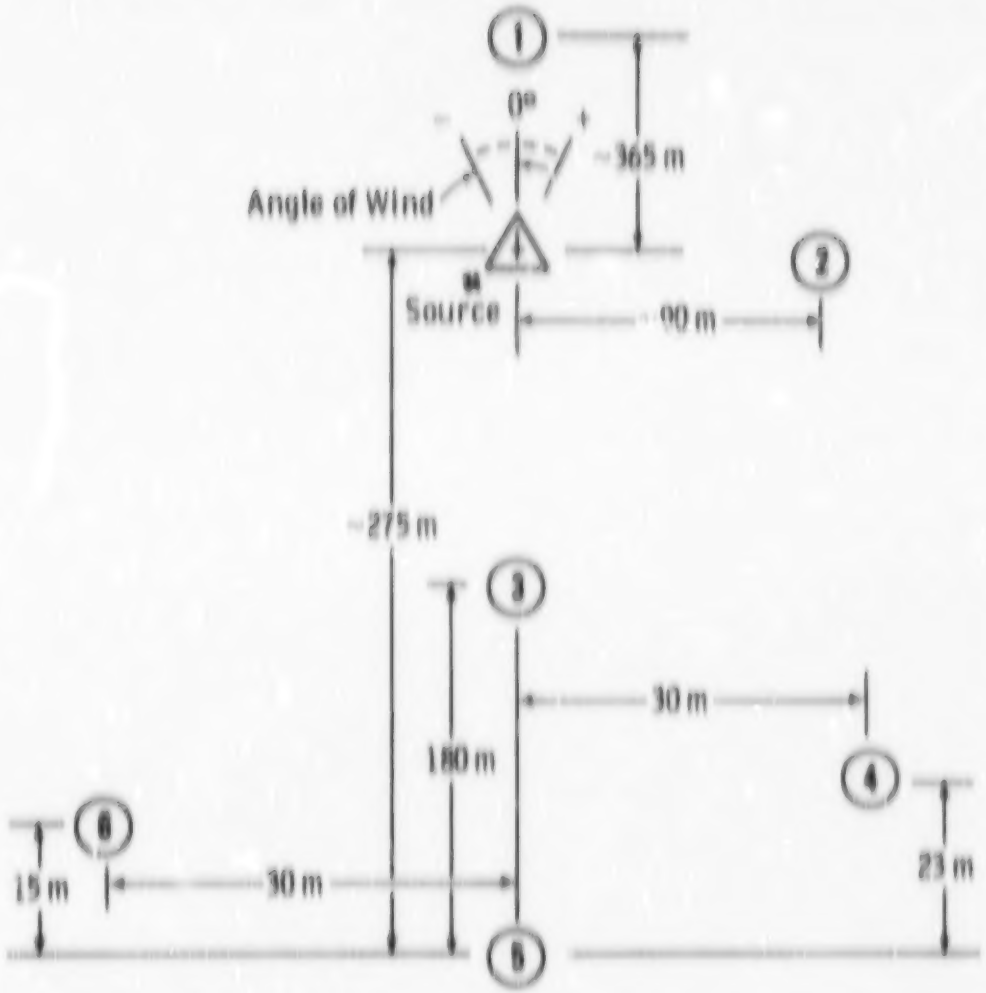

Figure 2. Ambient Air Sampling Arrangement Used For Sampling Stolle Corporation Site.

(1921.2 m^3) and 19.55 hours (1327.8 m^3) respectively.

The results from the analyses of the air samples are contained in Table 1. As expected, the highest total Cr concentration was obtained at Site 3, the nearest downwind centerline site located ~90 m from the Stolle plant. The upwind sampling Site 1 gave an indication of background values during the sampling period.

Table 1

Air Sampling Results

Sample Site No.	Total Conc. Cr ($\mu g/m^3$)
1 Array	0.02
1 Perimeter	0.05
2	0.010
3 Array	1.07
3 Perimeter	1.07
4	0.22
5	<0.01
6	<0.03

2.2 Water Samples

Water sampling sites were selected at the Stolle outfall and three points along the Great Miami River. The upstream site was ~30 m from the point where the treatment plant effluent enters the river, while the two downstream sites were located at approximately 3 and 6 streamwidths (~100 m and ~200 m) from that point. The numbers in black in Figure 1 represent the water sampling sites.

The water samples were collected on September 14-15, 1976. Samples of approximately 4 liters were collected at the sites. Suspended particulate samples were obtained by filtering the water samples through 0.45 μm Millipore® filters as described in Section 4.2 of the main report. Analyses were performed as described in Section 5.3 of the main report.

The results for the water analyses are shown in Table 2. As expected, the highest Cr concentration was obtained at the plant outfall (Site #2). However, in comparing the upstream (Site #1) with the downstream (Sites #3 and #4) river results there seems to be no significant increase in dissolved chromium concentrations in the river due to the Stolle outfall. The NPDES permit limits for chromium in the Stolle plant wastewater were:

Total Chromium	- daily average	450 ug/l
	- daily maximum	1050 ug/l
Chromium(VI)	- daily average	355 ug/l
	- daily maximum	940 ug/l

during the September 14-15, 1976 sampling period. The results obtained are within these limits. However, more stringent limitations were scheduled to go into effect on November 25, 1976 setting these new allowable levels:

Total Chromium	- daily average	500 ug/l
	- daily maximum	1000 ug/l
Chromium(VI)	- daily average	50 ug/l
	- daily maximum	100 ug/l

Had the new levels been in effect, the total chromium concentration of 580 ug/l at the plant outfall (Site #2) would have exceeded the allowable daily average. Stolle Corporation analysis reports showed an average total chromium concentration of 117 ug/l and an average chromium(VI) concentration of 46 ug/l during September 1976.

Table 2

Water Sampling Results

Sample	Total Cr (mg/l)	Cr(VI)(ug/l)
Site #1	<0.02	<0.1
Site #2	0.58	0.56
Site #3	<0.02	0.1
Site #4	0.03	<0.1

The values for total chromium in the suspended particulates from the water samples are given in Table 3. There is a definite contribution to the chromium content in river water particulates from the treatment plant effluent. This is shown by the higher downstream values (Sites #3 and #4) compared to the upstream value (Site #1). The higher value at Site #3 (0.14 mg/l) compared to the outfall at Site #2 (0.07 mg/l) indicates that either a significant portion of the chromium particulates are coming from the Guthrie Road treatment plant effluent, or the introduction of the outfall into the treatment plant effluent is causing some of the dissolved chromium to come out of solution producing higher particulate chromium values.

Table 3

Particulates in Water

Sample	Total Cr
Site #1	5 ug/l
Site #2	0.07 mg/l
Site #3	0.14 mg/l
Site #4	0.02 mg/l

2.3 Sediment Samples

Sediment samples were collected at the same sites as the water samples with the exception of the outfall (Site #2). Approximately 100 ml of sediment was scooped from the bottom of the river at Sites #1, #3, and #4 as described in Section 4.3 of the main report and analyzed as described in Section 5.2

The results from these analyses are given in Table 4. The results show no trend in the total chromium values.

Table 4

Sediment Sampling Results

Sample	Total Cr (ug/g)
Site #1	1.03
Site #3	0.81
Site #4	1.18

2.4 Soil Samples

The optimum soil sampling sites for the Stolle Corporation plant were chosen on the basis of the diffusion model described in Section 3.3 of the main report. This model indicated a maximum concentration area at 29° (relative to due north) and a secondary concentration area at 180°. The locations of the soil sampling sites are indicated by letters in Figure 1. These sites were

positioned relative to the center of the building on the Stolle Corporation site. Site A was located at 229° at a distance of ~ 100 m in a grassy field adjoining the Stolle site. This site was selected to provide a background measurement since it was not in an area of predicted high concentration. Sites B and C were chosen to sample the predicted area of maximum concentration and were located at 29° at distances of ~ 300 m and 100 m, respectively. Site B was located at the fence line of the Monsanto Research Corporation, Dayton Laboratory property along Nicholas Road. Site C was located in a gravelly area along the Stolle fence line. Sites D and E were chosen to sample the predicted secondary area of maximum concentration and were located at 180° at distances of ~60 m and 200 m, respectively. Site D was located in a grassy area at the south corner of the Stolle fence line near West River Road. Site E was located on the flood plain on the opposite side of the Great Miami River. The samples were collected and analyzed as described in Sections 4.3 and 5.2 of the main report. Duplicate samples were obtained and analyzed for selected sites.

The results from the analyses of the soil samples are given in Table 5. No noticeable pattern can be seen in the data.

Table 5

Soil Sampling Results

Sample		Total Chromium (µg/g)
Site A	Sample 1	24.3
	Sample 2	23.7
Site B	Sample 1	16.0
	Sample 2	-
Site C	Sample 1	15.9
	Sample 2	-
Site D	Sample 1	36.9
	Sample 2	12.9
Site E	Sample 1	-
	Sample 2	19.8

APPENDIX D

SAMPLING AND ANALYSIS OF CHROMIUM AT BREZNER TANNING COMPANY PENACOOK, NEW HAMPSHIRE

Brezner Tanning Company

Penacook, New Hampshire 03301

1. PRESAMPLING SURVEY

1.1 Description of the Plant Site

Bresner Tanning Company located in Penacook, New Hampshire, was chosen as a typical tanning operation suitable for chromium sampling. This particular tannery was chosen because its wastewater effluent is treated at a municipal sewage treatment plant that was included in a companion sampling study (Appendix G) making possible the examination of tannery effluent before and after treatment. No presampling survey visit was conducted. During the sampling visit of November 17-18, 1976, contact was made with Mr. Peter Fanny, Plant Manager and Mr. John Heffernan, Lab Supervisor who were very helpful and willing to cooperate with MRC personnel in the chromium sampling.

The tanning process uses a solution of chromium(III) sulfate, $Cr_2(SO_4)_3$, to cure the hides. Since this curing solution is purchased directly in solution form and not prepared, no air emissions (stack or fugitive) would be anticipated. Therefore, no soil samples or air samples for inorganic chromium were collected at the Bresner site.

The tannery occupies a site of approximately 75m x 45m. Two buildings are on the site - one contains offices and production facilities and the second serves as a warehouse and loading dock. The plant operates on a 5 day/week, 8 hour/day schedule. Since the tanning process is a batch operation, there are peaks in the plant wastewater effluent corresponding to the emptying of vats which usually occurs around mid-week (Wednesday).

The Bresner site is situated in the heart of the town of Penacook. It is bounded on the north by a two-lane paved road, a city operated wastewater neutralization facility, and a wooded area; on the east by the intersection of three two-lane paved streets, a parking lot, a church and numerous residences; on the south by more residences and small businesses; and on the west by a small river which empties into the Merrimack River, and U.S. Highway 3. Although another tannery in the area discharges waste to the same sewage treatment facility, it presented no potential interferences to the samples collected.

The wastewater effluent from the Bresner plant goes into a "super scooper" which is a crude on-site settling tank. From here the tannery wastes are pumped across the street to a city operated neutralization tank which uses a caustic neutralization process. After neutralization the wastewater is pumped a distance of ~0.8 km to the Penacook Municipal Sewage Treatment Plant. The sewage treatment plant wastewater is eventually discharged into the Merrimack River (see Appendix E). The tannery effluent amounts to ~3,000 m^3/day.

1.2 Description of the Surrounding Area

The Bresner Tanning Company is situated in the midst of the population concentration of Penacook, New Hampshire. Penacook is a town of ~3,000 people in a rural area approximately 9 km northwest of Concord, the capital of New Hampshire. It is situated on U.S. Highways 3 and 4 just west of Interstate 93. The general terrain is hilly and wooded with little industrial concentration.

2. SAMPLING AND ANALYSIS RESULTS

Sampling of the Brenner Tanning Company site was conducted on Wednesday and Thursday, November 17-18, 1976 to correspond to the expected peak chromium discharge associated with vat dumping. As stated earlier, no inorganic chromium air emissions were anticipated. Therefore, neither inorganic air samples nor soil samples were included in the study. However, one air sample was collected for "organic" chromium species. A sample of the plant wastewater effluent and a sample of sediment from a previously used outfall point on the Merrimack River were also collected.

2.1 Air Samples for "Organic" Chromium Species

An air sample was collected at a downwind site (Site #2, Figure 1) just across the street to the east of the plant about 25 m from the main building. This sample was taken to evaluate the possibility of volatile organochromium species in the air around the tannery site. The samples were collected by drawing air through an XAD-2 resin tube as described in Section 4.1 of the main report. Analysis was performed as described in Section 5.4.1. The results showed no detectable chromium (i.e., <0.2ug/m^3) in the air sample.

2.2 Water Sample

Since the tannery discharges its effluent directly into the treatment facility, only a sample of the plant effluent was collected. The sample was taken at the "super scooper" settling

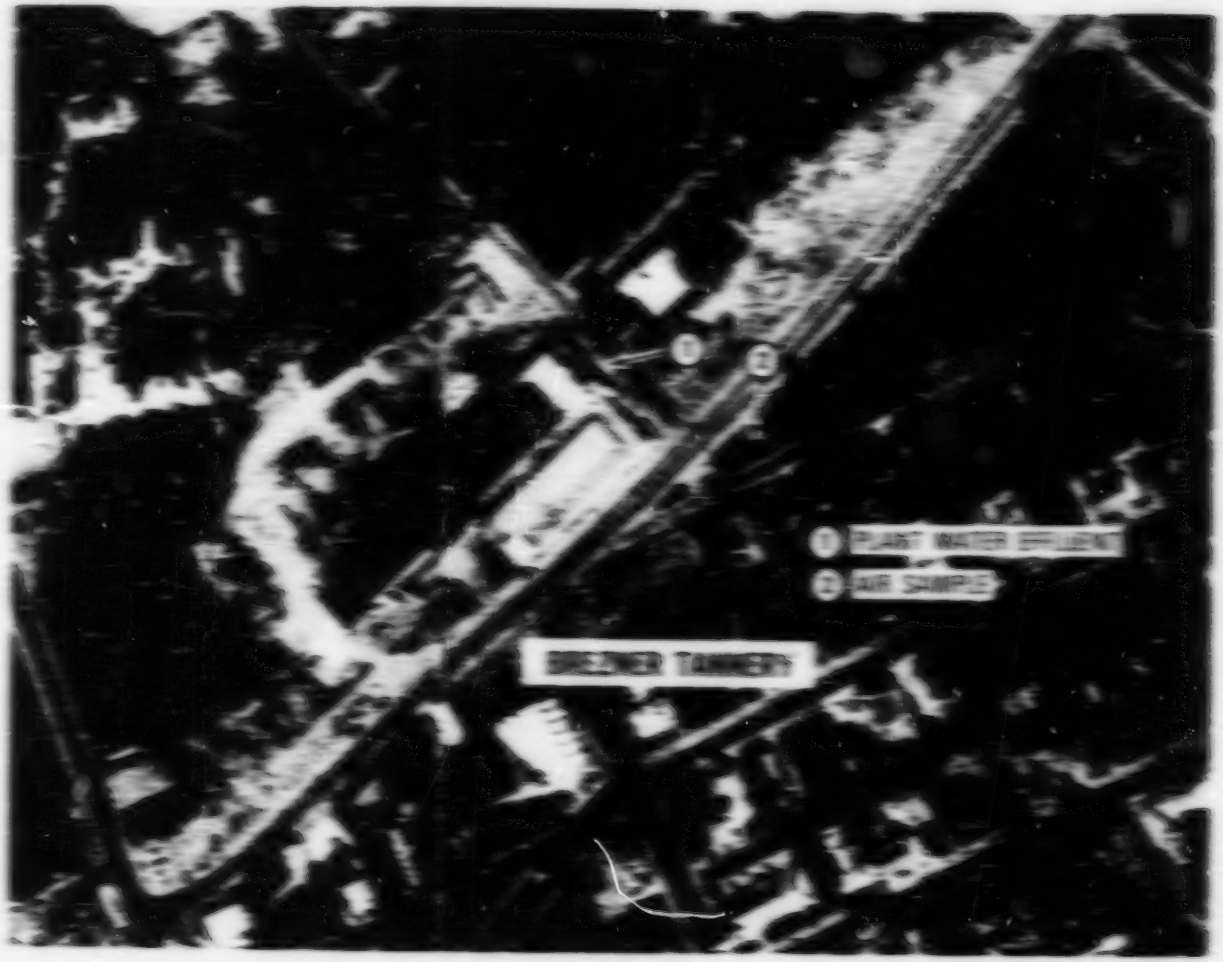

Figure 1. Aerial View of Brewster Tanning Company Site With Sampling Locations.

tank just before the wastewater is discharged across the street to the city wastewater neutralization facility (Site #1, Figure). The sample was a muddy gray color with a heavy loading of suspended solids and a pungent odor. The suspended particulates were collected by filtration through an 0.45 um Millipore® filter. Analyses for dissolved and suspended chromium were performed using the procedure described in Section 5.3 of the main report. The results are given in Table 1. About 80% of the total chromium emissions in the plant effluent are particulate in nature.

2.3 Sediment Samples

The Bresaner plant has been discharging its effluent into the municipal treatment plant for two years. Prior to this, the tannery effluent was discharged directly into the Merrimack River at a point not shown in Figure 1. Two sediment samples were collected at the old outfall site and analysed according to the procedure described in Section 5.2 of the main report. The results are given in Table 2. These results are similar to those obtained for the downstream sediment samples in the Penacook Sewage Treatment Plant studies (Appendix E).

Table 1

Effluent Sample Results

Type	Total Cr (mg/l)	Cr(VI) (mg/l)
Dissolved	2.3	0.097
Suspended	10.8	--

Table 2

Old Outfall Sediment Sample Results

Sample	Total Cr µg/g
1	14.8
2	10.9

APPENDIX B

SAMPLING AND ANALYSIS OF CHROMIUM AT PENACOOK MUNICIPAL SEWAGE TREATMENT PLANT PENACOOK, NEW HAMPSHIRE

Penacook Municipal Sewage Treatment Plant

Penacook, New Hampshire 03301

1. PRESAMPLING SURVEY

Telephone contacts were made on September 3 and 7, 1976 with Michael J. Obrien of the Region I EPA office in Boston, Massachusetts [(617)-223-5013] to determine a suitable municipal sewage treatment plant that receives tannery wastewater for evaluation in the sampling program. Through this process the sewage treatment plant of Penacook, New Hampshire was chosen, since it processed the effluent from the Bresner Tanning Company (see Section 2.2.4 of the main report and Appendix D).

A presurvey visit was made to Concord, New Hampshire on September 16, 1976 to consult with Mr. Ronald H. Ford, Director of Public Works, Concord, N.H. and Mr. Walter E. Norris, Wastewater Superintendant. The Penacook treatment plant is under their supervision. Mr. Ford and Mr. Norris were very cooperative in making arrangements for the sampling of the Penacook plant.

1.1 Description of the Plant Site

The Penacook Municipal Sewage Treatment Plant is located on the Merrimack River on the eastern edge of Penacook, New Hampshire. The facility is two years old and processes the wastewater from two tanneries in the area. The tannery effluents constitute ~80% of the total plant influent. The remaining 20% is municipal wastes. There is no other major industry in the area. The treatment plant has a capacity of ~16,000 m^3/day and was operating at ~60% capacity (~9,500 m^3/day) when sampling was conducted on November 18-19, 1976. The Penacook plant is a

secondary treatment facility with a wastewater retention time of 36 hours. Plant operation is continuous.

The overall plant site is large, occupying an area approximately 365 m x 180 m. The process area covers approximately 3 acres with the remaining portion primarily occupied by an old landfill that was formerly used for on-site sludge disposal. Currently the sludge is trucked to a regional sanitary landfill. The plant site is bounded on the north and east by the Merrimack River. The opposite bank is wooded. To the south is the landfill area and beyond that a wooded area. A railroad runs along the western boundary of the plant beyond which are a few houses and a farm. The population density increases to the west of the plant as one approaches the center of Penacook.

The treated plant effluent enters the river through an 91 m i.d. concrete pipe. The actual outfall is subsurface at a point 46 m from the river bank. At this point the river is large (45 m wide) and the contribution of the effluent to the total flow is small. There was no visible change of appearance in the river water at the outfall. No difference was observed in aquatic life and organic material above and below the outfall.

1.2 Description of the Surrounding Area

The Penacook Municipal Sewage Treatment Plant lies to the east of the major population center of Penacook, New Hampshire in a hilly and predominantly wooded area. Penacook is a town of approximately 3000 people located approximately 9 km northwest of Concord, the capital of New Hampshire. Two tanneries comprise the major industries of the area.

2. SAMPLING AND ANALYSIS RESULTS

The Pennsauk Municipal Sewage Treatment Plant site was sampled on Thursday and Friday, November 18-19, 1976. These days were chosen to evaluate the effectiveness of the treatment process for the removal of the peak chromium concentrations corresponding to the usual mid-week tannery vat dumping practices (see Appendix D). Since the treatment plant has a residence time of 36 hours, Thursday and Friday were chosen as optimum days for observing these effects.

No air samples for inorganic chromium were taken since no major source of particulate inorganic chromium air emissions was present. For this reason and also because the plant is relatively new (3 years old), no soil samples were collected. There is, however, a slight possibility for fugitive chromium emissions due to aeration operations used in the treatment process. Two air samples were taken to examine the possibility of volatile "organic" chromium species in the air around the treatment site. Water samples for both inorganic and "organic" chromium, sediment samples and sludge samples were collected. The details for the sampling and analyses are contained in the following subsections.

2.1 Air Samples for "Organic" Chromium Species

Samples were collected at sites A and B of Figure 1 for chromium species in air using XAD-2 resin tubes as described in Section 4.1 and Figure 6 of the main report. Site A was located over the treatment plant influent, and Site B was located over one of the aeration tanks. The sample tubes were analyzed according to the procedure described in Section 5.4.1 of the main

report. The results of those analyses are given in Table 1. Both values were below the detection limit of the method. The difference in the detection limits for the two sites (i.e., 0.3 $\mu g/m^3$ for Site A and 0.4 $\mu g/m^3$ for Site B) reflects the different sample sizes collected at the two sites (6.06 m^3 at Site A and 2.74 m^3 at Site B).

Table 1

Organic Chromium in Air Results

Sample	Total Cr ($\mu g/m^3$)
Site A	<0.3
Site B	<0.4

3.2 Water Samples

Water sampling sites were selected at three points along the west bank of the Merrimack River. Site #1 (Figure 1) was ~30 m upstream of the treatment plant outfall, while Sites #3 and #4 were ~30 m and ~60 m, respectively, downstream of the outfall. A sample of the plant effluent was taken at Site #2 at the point in the final settling tank where the effluent enters the pipe that discharges it into the river since the actual outfall is subsurface.

Four-liter samples were collected at each of the sites over a 24-hour period as described in Section 5.2 of the main report. The suspended particulates were removed by filtration through an 0.45 µm Millipore® filter to obtain a separate analysis of particulate vs. dissolved chromium. Analyses were performed as described in Section 5.3 of the main report.

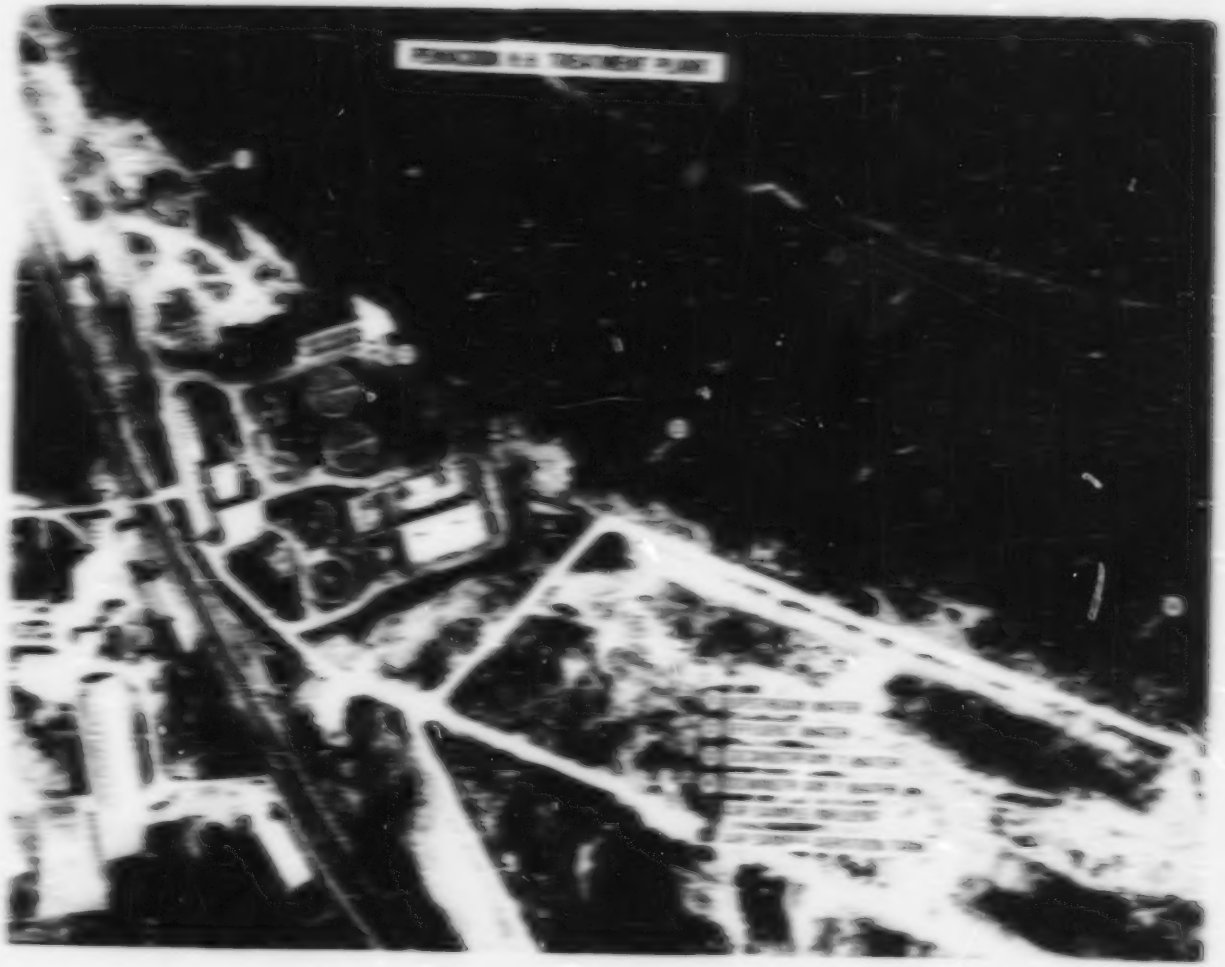

Figure 1. Aerial View of Penbrook Municipal Sewage Treatment Plant with Sampling Locations.

The results for the dissolved chromium analyses are shown in Table 2. As expected, the highest concentrations of both total chromium and chromium(VI) were obtained in the treatment plant effluent. The total chromium levels in the river water (Sites #1, #3, and #4) were below the detection limit of the technique (0.02 mg/l). A surprising result is the higher upstream value (Site #1) for chromium(VI) compared to those obtained at the downstream sites (Sites #3 and #4).

Table 2

Water Sampling Results

Sample	Total Cr (mg/l)	Cr(VI)(ug/l)
Site #1	<0.02	0.4
Site #2	0.05	1.3
Site #3	<0.02	0.1
Site #4	<0.02	<0.1

The results for the analyses of chromium in the suspended particulates are given in Table 3. Although the total chromium concentration in the plant effluent (Site #2) was 0.16 mg/l, no assessment could be made of its contribution to the total chromium in the particulate matter of the river water since the values obtained for these samples were either at or below the detection limit of the technique (0.5 ug/l).

Table 3

Particulates in Water

Sample	Total Cr
Site #1	<0.5 ug/l
Site #2	0.16 mg/l
Site #3	0.5 ug/l
Site #4	<0.5 ug/l

The total chromium (dissolved + particulate) in the plant effluent was 0.21 mg/l. This is within the NPDES permit limit for the Tonawanda facility which allows a monthly average of 0.269 mg/l and a maximum day average of 0.537 mg/l.

Three 8-liter water samples were drawn through XAD-2 resin tubes to sample for "organic" chromium species by the technique described in Section 4.2 of the main report. One sample was taken of plant effluent water and samples of river water were taken upstream and downstream of the plant outfall by this method. The ether extracts of these tubes were analysed by flameless atomic absorption as described in Section 5.4.1 of the main report. In each case the value obtained for total "organic" chromium was less than the detection limit of the technique (0.15 ug/l).

2.1 Sediment Samples

Sediment samples were collected at the upstream water collection site (Site #1) and the first downstream water collection site (Site #3) by scooping ~100 ml of sediment from the river bottom. No samples were taken at Site #2 (plant effluent) or Site #4 (the second downstream site). These samples were analysed by the technique described in Section 5.2 of the main report. The results are given in Table 4. These results show a definite increase in the chromium level in the river sediment as a result of the discharge of the treatment plant effluent.

Table 4

Sediment Sampling Results

Sample	Total Cr (ug/g)
Site #1	4
Site #3	23.0

3.4 Sludge Samples

A sample of sewage sludge was obtained from the digestors to determine its inorganic and "organic" chromium content. The sample was processed according to the extraction scheme outlined in Figure 8 of the main report. The results from the analyses of the inorganic fraction and the water soluble, base, strong acid, neutral and weak acid organic fractions are given in Table 5. Less than 1% of the total chromium in the sludge was ether extractable "organic" chromium. It is interesting to compare the results obtained for this sludge sample with those obtained for the sludge sample from the Guthrie Road Treatment Plant (Appendix F, Table 4). In both cases, the "organic" chromium content is less than 1% of the total chromium. However, the chromium concentration of the Penacook sludge is an order of magnitude higher than that of the Guthrie Road sludge.

Table 5

Sludge Sample Results

Fraction	Total Cr (ug/g in dry sludge)
Inorganic	13,950
Organic	
Water Solubles	0.63
Bases	5.85
Strong Acids	2.30
Neutrals	80.0
Weak Acids	12.1
Total Organics	100.9

APPENDIX F

SAMPLING AND ANALYSIS OF CHROMIUM AT GUTHRIE ROAD SEWAGE TREATMENT PLANT DAYTON, OHIO

Guthrie Road Sewage Treatment Plant
Guthrie Road
Dayton, Ohio 45418

1. PRESAMPLING SURVEY

1.1 Description of the Plant Site

The City of Dayton Guthrie Road sewage treatment plant, Guthrie Road, Dayton, Ohio 45418 was chosen for sampling because the City of Dayton Water Department personnel stated that the bulk of chromium waste they receive is handled by this facility. Contacts were made with Mr. Walton Farr, Director of the Department of Water, Mr. DePre Tossey, Superintendant of Wastewater Treatment, and Mr. John Barton, Plant Engineer to obtain permission for sampling and aid in locating the sampling sites.

A preliminary survey visit was made to the Guthrie Road treatment facility on December 17, 1976. The plant occupies a site of approximately 640 m x 1280 m. There are two major buildings on the site - one with offices and a laboratory and the second houses the control room and maintenance facilities. Various other small buildings, 20 large trickle bed filters and several large sludge pits are also located on the site.

The plant is bounded on the north by Guthrie Road, an open field and Mudden Golf Course, on the east by West River Road, an open field and the Great Miami River and on the south and west by open fields and wooded areas. The closest industry is on the opposite bank of the Great Miami River and consists of light industry, an asphalt batch plant, sand and gravel operations, and storage warehouses. No significant interferences are expected in the samples due to these operations in the area.

Guthrie Road sewage treatment plant handles waste from the City of Dayton and other sections of Montgomery County including Englewood and Trotwood. The major contributors of chromium in the wastewater processed by this facility are chrome platers and large industry such as General Motors and Inland installations in the area serviced. It should be noted that the chromium wastes processed by the Guthrie Road plant do not include any contribution from the Stolle Corporation since its wastewater is discharged into the processed effluent stream from the treatment plant (see Appendix C).

The plant operates continuously and discharges 190,000-240,000 m^3/day of treated wastewater through an open concrete ditch into the Great Miami River. The average water retention time in the plant is ~4.5 hours. The outfall is very turbulent and significantly affects the flow of the river at the point of entry and for some distance downstream as can be seen in the aerial photo (Figure 1) which shows the effluent stream at Site #3. A number of dead and incapacitated fish were observed below the outfall. However, vegetation is plentiful and several people were fishing in the area.

1.2 Description of Surrounding Area

The City of Dayton Guthrie Road Sewage Treatment Plant is located in the southwestern metropolitan Dayton, Ohio area approximately 16 km south of the intersection of Interstates 70 and 75. The immediate area around the plant site has a relatively low population concentration which increases as one moves toward the Dayton population center. The City of Dayton is located in a river valley at the junction of the Miami, Mad, and Stillwater Rivers. The general topography is flat. The metropolitan area has a population of ~865,000 and supports an impressive diversity of industry. There are some 850 plants located in Montgomery County producing over 1000 products with an estimated value of over

$1 billion. Major industries in the area include automotive subassembly, appliance manufacturing and precision equipment.

2. SAMPLING AND ANALYSIS RESULTS

Due to the nature of the operation at the Guthrie Road plant, no inorganic chromium emissions were anticipated. This eliminated the necessity of collecting soil samples and air samples for inorganic chromium. However, air samples for "organic" chromium species, water and sludge samples were collected at the site on January 5-6, 1977.

2.1 Air Samples for "Organic" Chromium Species

Air samples were collected at sites #4 and #5 of Figure 1 using the technique for "organic" chromium species described in Section 5.1 and Figure 6 of the main report. Site #4 was downwind of the trickle bed filters and Site #5 was over one of the sludge ponds. These samples were analysed by the procedure described in Section 5.4.1 of the main report. The data obtained from these analyses are contained in Table 1. Both samples produced chromium concentrations less than the detection limit of 0.2 ug/m^3.

2.2 Water Samples

Samples of the plant influent (Site #1), the trickle bed filter recycle water (Site #2), and the plant effluent (Site #3) were collected using the methods described in Section 4.2 of the main report. The trickle bed filter recycle water is part of the effluent (~63%) that is returned through the trickle bed filters. The effluent sample was taken upstream of the point where the Stolle outfall enters the effluent stream. Four-liter samples were collected at each site over a twenty-four hour period,

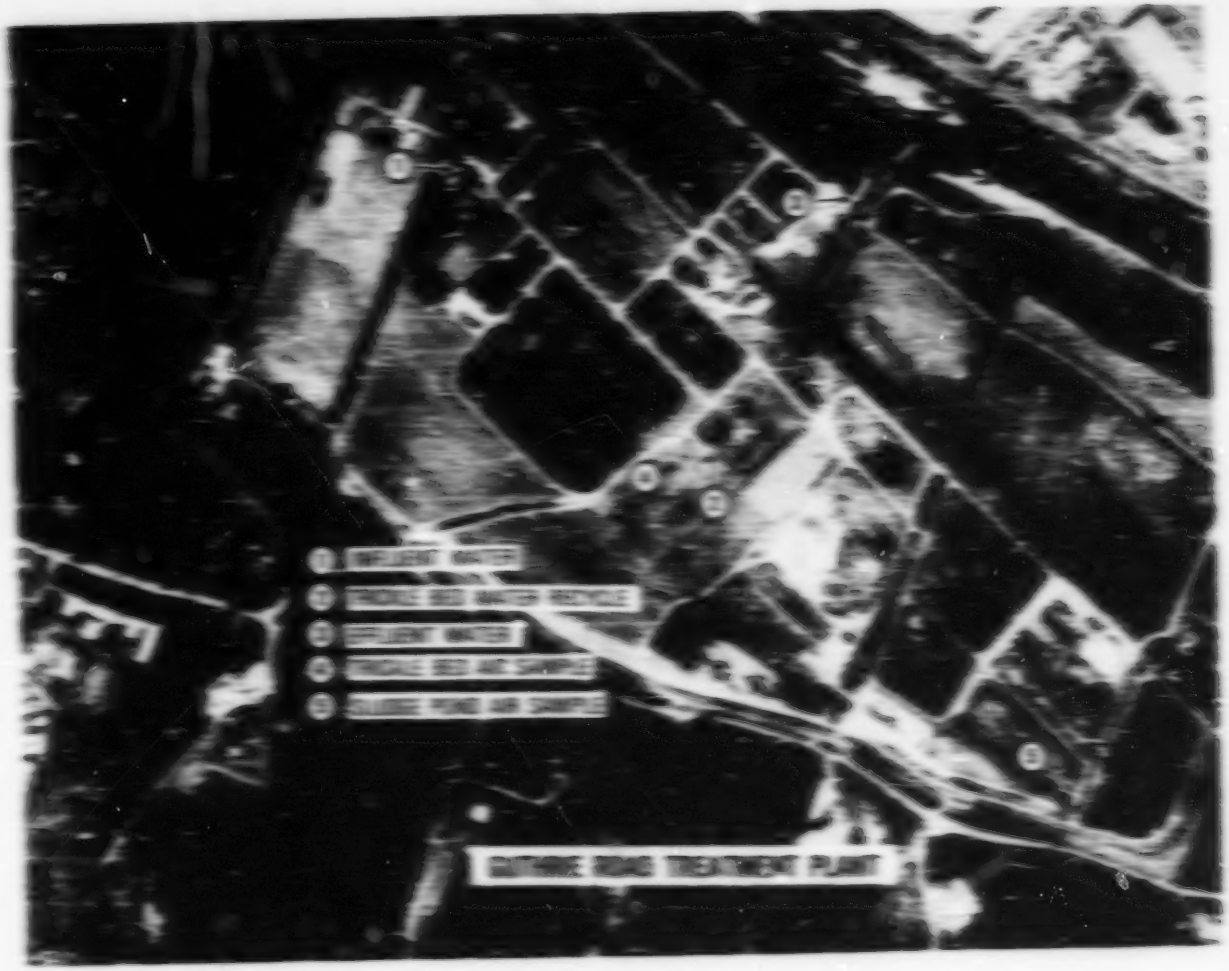

Figure 1. Aerial View of Guthrie Road Sewage Treatment Plant With Sampling Locations.

The influent and effluent waters were heavily loaded with suspended particulates. The particulates were removed for analysis by filtration through 0.45 µm Millipore® filters.

Table 1

Air Sample Results for "Organic" Chromium Species

Sample	Total Cr(ug/m³)
Site #6, Trickle Bed Filters	<0.2
Site #5, Sludge Pond	<0.2

The filtered water samples were analysed for dissolved chromium according to the procedure described in Section 5.3 of the main report. The results of these analyses (Table 2) indicate a significant reduction in dissolved chromium during the treatment plant processing. Of particular significance is the reduction of the highly toxic chromium(VI) content from 0.8 µg/l to below the detection limit (<0.1ug/l) during passage through the treatment plant.

Table 2

Water Sampling Results

Sample Location	Total Cr (mg/l)	Cr(VI) (ug/l)
Site #1, Influent	0.04	0.8
Site #3, Effluent	0.02	<0.1
Site #2, Trickle Bed Recycle	0.04	<0.1

The results for the chromium analyses of the suspended particulate samples are contained in Table 3. These indicate a reduction in particulate chromium during passage through the treatment plant.

There is some inconsistency in the results, however, due to the lower chromium concentration (26.4 ug/l) in the trickle bed filter recycle water compared with the effluent water (56.9 ug/l). One might normally expect these results to be higher than or equal to the effluent values. This would indicate that perhaps the particulate chromium concentration is increased on recycling through the trickle bed filters.

The results for total chromium (dissolved + particulate) in plant influent and effluent obtained in this study (132.6 ug/l and 76.9 ug/l, respectively) compare well with values of 181 ug/l and 72 ug/l reported by plant officials in July 1976. These were described as "typical" values.

Table 3

Particulates in Water

Sample Location	Total Cr (ug/l)
Site #1, Influent	92.6
Site #3, Effluent	56.9
Site #2, Trickle Bed Recycle	26.4

Sites along the Great Miami River below the treatment plant outfall were not sampled during this study because such results would represent a composite for the treatment plant and Stolle Corporation effluents since the Stolle outfall is introduced into the treatment plant effluent water. Sampling of the river was conducted during the Stolle site studies (Appendix C) and these figures give some indication of the combined effect of the treatment plant and Stolle effluents on the chromium content of the river water, suspended particulates, and sediment.

3.3 Sludge Samples

A sample of sewage sludge was obtained from the digestors and processed according to the ether extraction scheme outlined in Figure 8 of the main report. This scheme produces an inorganic fraction, and an organic fraction that is further fractionated into water soluble, base, strong acid, neutral, and weak acid fractions. The results for the total chromium in each of these fractions are given in Table 4. Slightly less than 1% of the total chromium in the sludge sample was in the form of other soluble chromium species.

Table 4

Sludge Sample Results

Fraction	Total Chromium (ug/g in dry sludge)
Inorganic	911.0
Organic	
Water Solubles	1.58
Bases	0.38
Strong Acids	1.02
Neutrals	3.84
Weak Acids	1.79
Total Organics	8.57